

Optimal Tooltip Trajectories in a Hydrogen Abstraction Tool Recharge Reaction Sequence for Positionally Controlled Diamond Mechanosynthesis

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The use of precisely applied mechanical forces to induce site-specific chemical transformations is called positional mechanosynthesis, and diamond is an important early target for achieving mechanosynthesis experimentally. A key step in diamond mechanosynthesis (DMS) employs an ethynyl-based hydrogen abstraction tool (HAbst) for the site-specific mechanical dehydrogenation of H-passivated diamond surfaces, creating an isolated radical site that can accept adatoms via radical-radical coupling in a subsequent positionally controlled reaction step. The abstraction tool, once used (HAbstH), must be recharged by removing the abstracted hydrogen atom from the tooltip, before the tool can be used again. This paper presents the first theoretical study of DMS tool-workpiece operating envelopes and optimal tooltip trajectories for any positionally controlled reaction sequence-and more specifically, one that may be used to recharge a spent hydrogen abstraction tool-during scanning-probe based ultrahigh-vacuum diamond mechanosynthesis. Trajectories were analyzed using Density Functional Theory (DFT) in PC-GAMESS at the B3LYP/6-311G(d,p)//B3LYP/3-21G(2d,p) level of theory. The results of this study help to define equipment and tooltip motion requirements that may be needed to execute the proposed reaction sequence experimentally and provide support for early developmental targets as part of a comprehensive near-term DMS implementation program.

Keywords: Abstraction, Carbon, Diamond, DMS, Germanium, Hydrogen, Mechanosynthesis, Nanotechnology, Pathology, Positional Control, Reaction Sequence, Tooltip, Trajectory.

CONTENTS

1.	Introduction	1
2.	Computational Methods	4
3.	Reaction I: Join GeRad Tool to Apical Ethynyl C Atom	
	of HAbstH	5
	3.1. Tooltip Geometry and Coordinate System	5
	3.2. PES as a Function of Positional Angles φ and θ	6
	3.3. Trajectory Pathologies of Reaction I	8
	3.4. PES as a Function of Rotational Angle ρ	9
	3.5. Lateral Displacement Error Tolerance	10
	3.6. Optimal Tooltip Trajectories	11
4.	Reaction II: Abstract Apical H from HAbstH Using	
	GeRad2 Tool	15
	4.1. Tooltip Geometry and Coordinate System	15
	4.2. PES as a Function of Positional Angles $\varphi_{\rm H}$ and $\theta_{\rm H}$	16
	4.3. Trajectory Pathologies of Reaction II	18
	4.4. PES as a Function of Rotational Angle $\rho_{\rm H}$	20

1. INTRODUCTION

Arranging atoms in most of the ways permitted by physical law is a fundamental objective of molecular manufacturing. A more modest and specific objective is the ability to synthesize atomically precise diamondoid structures using positionally controlled molecular tools. Such

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1

^{4.6.} Optimal Tooltip Trajectories 21 5. Reaction III: Detach GeRad Tool from Recharged HAbst Tool. 21 5.1. Tooltip Geometry and Coordinate System 21 5.2. PES as a Function of Rotational Angle $\rho_{\rm D}$ 22 5.3. PES as a Function of Positional Angles $\varphi_{\rm D}$ and $\theta_{\rm D}$ 23 5.4. Trajectory Pathologies of Reaction III 23 5.5. Optimal Tooltip Trajectories 27 28 28 28

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Optimal Tooltip Trajectories in a Hydrogen Abstraction Tool Recharge Reaction Sequence



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REVIEW



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positional control might be achieved using an instrument like a Scanning Probe Microscope (SPM). The landmark experimental demonstration of positional atomic assembly occurred in 1989 when Eigler and Schweizer¹ employed an SPM to spell out the IBM logo using 35 xenon atoms arranged on nickel surface, though no covalent bonds were formed.

The use of precisely applied mechanical forces to induce site-specific chemical transformations is called positional mechanosynthesis. In 2003, Oyabu et al.² achieved the first experimental demonstration of atomically precise purely mechanical positional chemical synthesis on a heavy atom using only mechanical forces to make and break covalent bonds, first abstracting and then rebonding a single silicon atom to a silicon surface with SPM positional control in vacuum at low temperature. Using an atomic force microscope the same group similarly manipulated individual Ge atoms in 2004³ and Si/Sn atoms in 2008.⁴

The assumption of positionally controlled highly reactive tools operating in vacuum permits the use of novel and relatively simple reaction pathways. Following early general proposals by Drexler⁵ and Merkle⁶ for possible diamond mechanosynthesis (DMS) tools and sketches of conceptual approaches to a few reaction pathways, a comprehensive three-year DFT-based (Density Functional Theory) study by Freitas and Merkle⁷ computationally analyzed for the first time a complete set of DMS reactions and an associated minimal set of nine specific DMS tooltips that could be used to build basic diamond, graphene (e.g., carbon nanotubes), and all of the tools themselves including all necessary tooltip recharging reactions. Their work defined 65 foundational DMS reaction sequences incorporating 328 reaction steps.

A key step in the process of atomically precise mechanosynthetic fabrication of diamond is to remove a hydrogen atom from a specific lattice location on the diamond surface, leaving behind a reactive dangling bond able to accept adatoms via radical-radical coupling in a subsequent positionally controlled reaction step. This removal could be done using a hydrogen abstraction tool⁸ that has a high chemical affinity for hydrogen at one end but is elsewhere inert. The tool's unreactive region serves as a handle or handle attachment point. The tool would be held by a high-precision nanoscale positioning device such as an SPM tip that is moved directly over particular hydrogen atoms on the surface. One suitable molecule for a hydrogen abstraction tooltip is the acetylene or "ethynyl" radical, comprised of two triple-bonded carbon atoms. One carbon of the two serves as the handle connection and would bond to a nanoscale positioning device through a larger handle structure. The other carbon of the two has a dangling bond where a hydrogen atom would normally be present in a molecule of ordinary acetylene (C_2H_2) , forming the reactive tip. The environment around the tool would be inert (e.g., vacuum or a noble gas such as xenon). This tool has received substantial theoretical study and computational validation,⁵⁻¹⁴ and site-specific hydrogen abstraction from crystal surfaces, though not purely mechanical abstraction, has also been achieved experimentally via scanning probe microscopy. For example, Lyding et al.¹⁵⁻¹⁷ demonstrated the ability to abstract an individual hydrogen atom from a specific atomic position in a covalently-bound hydrogen monolayer on a flat Si(100) surface, using an electrically-pulsed SPM tip in ultrahigh vacuum. Ho's group¹⁸ has similarly demonstrated positionally controlled single-atom hydrogen abstraction experimentally using an SPM.

After each use, the "spent" hydrogen abstraction tool has an unwanted H atom bonded to its tip that must be removed before the tool can be used again for hydrogen abstraction in a molecular manufacturing system. Freitas and Merkle⁷ describe a mechanosynthetic reaction sequence (Fig. 1) labeled "RS5" involving three reaction steps that could be used to recharge a spent ethynyl-type hydrogen abstraction tool (hereinafter "HAbst" after recharge, "HAbstH"



Fig. 1. Schematic of reaction sequence 5 from Freitas and Merkle,⁷ showing recharge reaction for 1-ethynyladamantane hydrogen abstraction tool (end product of Reaction III, structure at top) using sequence of three positionally controlled reactions involving two 1-germanoadamantane radical tooltips. (C = black, H = white, Ge = yellow).

when hydrogenated and requiring recharge), modeled as an ethynyl radical mounted on an adamantane base (i.e., 1-ethynyladamantane). This base would be part of a larger diamond lattice handle structure in an actual DMS tool. The recharge reaction requires the use of a second positionally controlled tool, a germanium radical (hereinafter "GeRad"), which is modeled as an adamantane base with an unterminated germanium atom substituted for carbon at a bridgehead position (i.e., 1-germanoadamantane). The unterminated Ge atom is the active tip of the GeRad tool. During the recharge reaction RS5, the Ge radical on a GeRad tool is first bonded to the distal C atom of the ethynyl group on the spent HAbstH tool. A second GeRad (hereinafter "GeRad2") is brought up to the transactional H atom on the HAbstH tool and abstracts the H atom; this H atom is readily donated to a clean diamond surface (not illustrated), recovering the original GeRad2 tool. GeRad is then mechanically debonded from the distal C atom, yielding a recharged HAbst tool.

While the proposed recharge reaction sequence appears energetically favorable, to date the positional and rotational operating envelopes of specific DMS tools acting on specific surfaces, workpieces, or other tools have been examined theoretically in only one prior study¹⁹ that considered a C_2 dimer placement tool (DCB6Ge)²⁰ interacting with a clean C(110) diamond surface in a single mechanosynthetic reaction. No such studies have yet been attempted for any other DMS tool or deposition surface, nor have any yet been attempted for complete reaction sequences. This paper presents the first theoretical study of DMS tool-workpiece operating envelopes and optimal tooltip trajectories for any positionally controlled reaction sequence-in particular, one that may be used in a complete three-reaction mechanosynthetic sequence to recharge a spent hydrogen abstraction toolduring scanning-probe based ultrahigh-vacuum diamond mechanosynthesis. The results of this study help to define equipment and tooltip motion requirements that may be needed to execute the proposed reaction sequence experimentally and provide guidance on early development targets as part of a comprehensive near-term DMS implementation program.

2. COMPUTATIONAL METHODS

All studies were conducted using Density Functional Theory (DFT) in the PC-GAMESS version²¹ of the GAMESS (US) QC package^{21A} running on several clusters consuming ~188,320 CPU-hours of runtime at 1 GHz, and included 5,284 separate valid-structure calculations. During this four-year course of work (in 2005–2009) the hardware was upgraded several times, and has included a cluster of 3 GHz Pentium4 HT (5 nodes), a cluster of 2 GHz AMD Opteron machines (16 nodes) and 1.8 GHz Intel Xeon machines (8 nodes) at the Supercomputing Center at the Kazan Scientific Center of the Russian Academy of Sciences (KSC RAS), and a cluster of 1.6 GHz AMD Opteron 240 machines (8 nodes, 2 CPU per node).

A comparison (Table I) of the reaction energy (energy of optimized product (HAbstH-GeRad complex) less energy of optimized reactants) for Reaction I shows that computed exoergicity is dependent on basis set choice,

Table I. Comparison of basis sets for calculating bond lengths, bond angles, and reaction energies (without zero-point correction) in Reaction I.

Basis set	Reaction energy (eV)	C–Ge bond length (Å)	Ge–C–C bond angle (deg)
AM1	-0.708	1.974	122.7
STO-3	-2.109	1.918	120.7
MIDI	-1.135	1.953	123.8
3-21G(d)	-0.917	1.980	121.2
3-21G(2d,p)	-0.997	1.967	122.3
3-21G + (2d,2p)	-1.047	1.966	123.4
6-31G(d)	-1.083	1.953	123.4
6-31G + (2d, 2p)	-0.964	1.958	123.1
DZV	-1.234	1.953	125.6
6-311G	-0.695	1.969	123.8
6-311G(d,p)	-0.694	1.971	123.5
6-311G(d,p)//3-21G(2d,p)	-0.696	1.966 ^a	123.4 ^a
aug-cc-VTZ//6-311G(d,p)	-0.634	1.971^{b}	123.5^{b}
-			

^aGeometry from 3-21G(2d,p) basis set. ^bGeometry from 6-311G(d,p) basis set.

but that DFT energies computed using 6-311G(d,p)//3-21G(2d,p) differ little from 6-311G(d,p)//6-311G(d,p) and are comparable to the highest-accuracy cc-aug-VTZ//6-311G(d,p) energy, with semi-empirical AM1 giving a surprisingly good performance. Optimized reactant and product structures are also very similar to the 6-311G(d,p) results except for STO-3G. Based on these results, we selected the 6-311G(d,p)//3-21G(2d,p) basis set for the rest of this study, using B3LYP which is a hybrid Hartree-Fock/DFT method using Becke's three-parameter gradient-corrected exchange functional (B3)²³ with the Lee-Yang-Parr correlation functional (LYP).²⁴ The mean absolute deviation from experiment (MAD) for B3LYP/6-311+G(2d,p)//B3LYP/3-21G(d) energies is estimated²⁵ as 0.14 eV for carbon-rich molecules, which should be adequate for the purposes of this analysis while conserving computational resources, and which appears slightly superior to the MAD of 0.34 eV estimated²⁵ for the more commonly reported B3LYP/6-31G(d)//B3LYP/6-31G(d) basis set. In conventional positionally uncontrolled chemistry, errors on the order of 0.14 eV might well influence reaction rates and also the dominant reaction pathway taken when multiple alternative reaction pathways are present. However, in the context of the present analysis this should not be an issue because alternative reaction pathways are limited by using positional control. Zero-point corrections are not made to the energy data because:

(1) the differences between energies with and without a correction are small (~ 0.008 eV for Reaction I, and similarly for Reaction II),

(2) the number of points to be evaluated is large (many thousands in this study), and

(3) the computational expense is huge (e.g., analytical second derivatives for spin-unrestricted calculations are not implemented in PC-GAMESS and the calculation of numerical frequencies requires about twice as much CPU time as geometry optimizations).

For each of the three positionally controlled mechanosynthetic reactions examined, the HAbst, HAbstH and GeRad tooltips are constrained by fixing the positions of the three sidewall carbon atoms (CH₂ groups) in the tooltip adamantane base that are located on the side of the cage farthest from the active radical site of the tool. Each tool was thus fixed precisely in space by constraining just 3 toolbase atoms from the start of each run, then the system was allowed to relax to its equilibrium geometry during the run. This method provides the best model for anticipated actual laboratory conditions in which an experimentalist will control tooltip position by applying forces through a larger diamond lattice handle structure affixed behind the base structures of the respective tooltips. For each run, each tooltip base was positionally constrained to a specific spherical coordinate φ (in XY plane) and θ (in Z direction) in fixed increments, and to several fixed radial distances R, and the incoming tooltip was also constrained to a specific axial rotational angle ρ .

3. REACTION I: JOIN GeRad TOOL TO APICAL ETHYNYL C ATOM OF HAbstH

In Reaction I of the HAbst recharge reaction sequence RS5 (Fig. 1), a GeRad tool is brought up to the distal ethynyl carbon atom to which the abstracted hydrogen atom is bonded on the HAbstH tool (which now becomes the workpiece), and is then bonded. This decreases the carbon–carbon bond order from 3 to 2, causing the carbon dimer to become nonlinear relative to the adamantane handle central axis and creating an open radical site on the carbon atom proximal to the HAbstH base structure.

After defining the tooltip geometry and coordinate system for Reaction I (Section 3.1) we calculate the reaction PES (potential energy surface) as a function of positional angles φ and θ (Section 3.2), describe some trajectory-related pathologies (Section 3.3), calculate the reaction PES as a function of rotational angle ρ of the incoming GeRad tool (Section 3.4), estimate the tolerance for lateral displacement error in tooltip positioning for Reaction I (Section 3.5), then recommend some optimal GeRad tooltip trajectories for this reaction (Section 3.6).

3.1. Tooltip Geometry and Coordinate System

The tooltip geometry and coordinate system for Reaction I is shown in Figure 2. The first coordinate origin O is defined as the point equidistant from the fixed carbon atoms C4, C6, and C10 in the HAbstH adamantane base, and lying in the plane containing those atoms. The X axis lies perpendicular to the C4/C6/C10 plane and points from origin O to a second origin O' which is initially coincident with atom C12 in HAbstH, \sim 5.262 Å away from O. This axis passes from origin O through atoms C1, C11, C12, and H28, whose equilibrium positions are collinear in HAbstH. The Y axis originates at O', lies perpendicular to the X axis, and runs parallel to a vector pointing from atom C10 to origin O. The Z axis also originates at O' and lies perpendicular to X and Y axes following the right-hand rule, running parallel to a vector pointing from atom C6 to atom C4. The approaching GeRad tool is initially oriented relative to the HAbstH workpiece such that a line extending backwards through atoms C12 (origin O') and Ge35 perpendicularly penetrates the plane defined by the 3 fixed GeRad tool base carbon atoms (C30, C32, and C34), intersecting a third origin O" which lies in the C30/C32/C34 plane and is equidistant from C30, C32 and C34, analogous to origin O.

In this spherical coordinate system, φ is defined as the angle from the X axis to the Y axis of the projection of the vector pointing from O' to O" onto the XY plane. Note that $+\varphi$ is defined as rotation toward the -Y axis in the arrow direction, since the target hydrogen atom (H28) moves away from GeRad in the +Y direction ($-\varphi$ direction) upon GeRad bonding to atom C12 at the completion of



Fig. 2. Coordinate system for Reaction I: Positionally controlled reactant tooltips prior to reaction (top left), and following completion of reaction (top right), defining phi (φ) and theta (θ), including atom labels (bottom, left), and definition of tooltip axial rotation angle rho (ρ) (bottom, right). (C = yellow, H = blue, Ge = white).

Reaction I. θ is defined as the angle from the XY plane to the vector pointing from O' to O'', with $-90^{\circ} \le \theta \le +90^{\circ}$ and $-180^{\circ} \le \varphi \le +180^{\circ}$. Radial distance R is defined as the distance between origins O" and O'. Although atom C12 moves away from O' as the reaction proceeds, the proper experimental protocol is nevertheless to aim the O"to-Ge35 vector directly toward the fixed origin O' (not to C12, which moves) to execute Reaction I. The rotational state of HAbstH is completely specified after labeling the base atoms C4, C6, and C10 and defining the positive Y-axis as the C10-to-O direction. The rotational state of GeRad, specified by ρ , is measured as the angle taken from the O-to-C10 vector to the O"-to-C34 vector when GeRad is virtually repositioned to $(\varphi, \theta) = (180^\circ, 0^\circ)$ making O'' coincident with O, with $+\rho$ taken in the clockwise direction as viewed from O'. Thus, rotation to $+\varphi$ becomes equivalent to rotation to $-\rho$ at $\theta = +90^\circ$, or to $+\rho$ at $\theta =$ -90° . This coordinate system was chosen because origins O and O" experience negligible reaction-mediated nonthermal displacement during the course of the reaction and thus may be most directly controlled in an experimental apparatus.

3.2. PES as a Function of Positional Angles φ and θ

The PES as a function of positional angles φ and θ is shown in Figure 3, holding GeRad at the rotational angle $\rho = +40^{\circ}$, for four different tooltip-workpiece displacements (R = 5.60 Å, 5.35 Å, 4.85 Å, and 4.35 Å) as the GeRad tool approaches the HAbstH workpiece.

At R = 5.60 Å, with Ge35 roughly 3.20 Å away from O' (originally at C12), the PES in a $90^{\circ} \times 90^{\circ}$ angular region centered on $(\varphi, \theta) = (0^\circ, 0^\circ)$ is largely featureless and flat, with strongly endoergic mountains centered on $(\varphi, \theta) = (\pm 180^\circ, 0^\circ)$ due to rapidly rising steric repulsion between approaching HAbstH and GeRad tool handles at those angles. At R = 5.35 Å, with Ge35 roughly 2.95 Å away from O', a weakly endoergic hill about 30° in radius has appeared at the center of the PES due to rising repulsion between the Ge35 radical on the GeRad tool and the target hydrogen atom H28 on the HAbstH workpiece, since H28 lies between Ge35 and C12 at these angles of approach. At R = 4.85 Å, with Ge35 roughly 2.45 Å away from O', the hydrogen hill at the center of the PES has become more repulsive, defining an annular region surrounding the hydrogen hill within which the GeRad tool











Fig. 3. PES for Reaction I (endoergic = blue, exoergic = red, energy in eV) as a function of tooltip positional angles $\varphi = -180^{\circ}$ to $+180^{\circ}$, $\theta = -90^{\circ}$ to $+90^{\circ}$, at tooltip separation distances R = 5.60 Å, R = 5.35 Å, R = 4.85 Å and R = 4.35 Å, and GeRad rotational angle $\rho = +40^{\circ}$, with labeled isoergic contours. Energy minima are marked with solid dots at (φ , θ) = (-46° , $+74^{\circ}$) (-0.506 eV) and ($+34^{\circ}$, $+74^{\circ}$) (-0.504 eV) at R = 4.85 Å, (φ , θ) = (-23° , $+26^{\circ}$) (-0.486 eV) and ($+24^{\circ}$, $+26^{\circ}$) (-0.482 eV) at R = 4.35 Å.

may approach the distal C12 atom along a maximally exoergic trajectory. By R = 4.35 Å, with Ge35 roughly 1.95 Å away from O' (the approximate equilibrium Ge–C bond length), H28 has moved off to the side and the PES in an $80^{\circ} \times 80^{\circ}$ region centered on (φ , θ) = (0° , 0°) is uniformly exoergic, mostly in the -0.40 to -0.50 eV range, for the completed Ge35–C12 bonding reaction.

The spherical representations of the PES (Fig. 4) for R = 4.85 show regions of favorable (red, exoergic) and unfavorable (blue, endoergic) net reaction energies from the viewpoint of a GeRad tool as it approaches the HAbstH tool—here represented by the hydrogenated ethynyl (CCH) group, the HAbstH handle bridgehead C atom to which the ethynyl is attached and the three sidewall C atoms attached to the bridgehead. The central endoergic (blue) hydrogen hill is surrounded by an exoergic (red) annular region, with another (blue) annular region behind it indicating unfavorable energetics, with a yellow region at negative X-axis values that is excluded due to handle collision.

A comparison of the succession of charts in Figure 3 indicates the presence of a favorable annular region within which many dozens of useful approach trajectories exist, such as the $(\varphi, \theta, \rho) = (+40^\circ, +70^\circ, +40^\circ)$ example. A closer examination of the progression of the Ge35-C12 bonding reaction for this exemplar trajectory (Fig. 5) shows the kinking of the bridgehead-ethynyl group and the $\sim 60^{\circ}$ shift in CC–H28 bond angle (left image), along with the ~ 0.13 Å increase in CC bond length as bond order changes from 3 (C=C) to 2 (C=C) and the change in Ge35-C12 equilibrium separation as the Ge-C bond forms (center image). The 1D PES (right image) shows a slight uplift in energy peaking at R = 5.65 Å as GeRad approaches, prior to consummation of the bonding reaction, revealing a small +0.09 eV reaction barrier along this trajectory. The ~ 0.18 Å excess separation (above diagonal line on top curve in center image) due to repulsion between Ge35 and C12 at the R = 5.65 Å barrier peak implies that only a rather modest mechanical force of ~0.80 nN must be applied by the incoming GeRad tool to overcome this

repulsive barrier, when following this particular exemplar approach trajectory.

3.3. Trajectory Pathologies of Reaction I

Aside from the known possible reaction pathologies of Reaction I that are energetically disfavored,⁷ two additional classes of undesired trajectory-associated pathologies have been identified in the present work (Fig. 6).

The first trajectory pathology involves the bonding of Ge35 and C11 (the proximal ethynyl carbon atom on HAbstH to which H28 is not directly attached) in the case of high- φ trajectories that allow the Ge35 radical site to pass too close to C11 while moving toward C12, enabling an unwanted Ge35-C11 bond to form before the desired Ge35–C12 bond can form (Fig. 6(A)). Nonexhaustive investigations of numerous relevant (φ , θ) trajectories at $\rho = +40^{\circ}$ and R = 4.85 Å revealed that the Ge35–C11 misbonding pathology does not occur for $|\varphi| \leq 90^\circ$, and occurs only at low θ for some higher values of φ , e.g., at $(\varphi, \theta) = (-100^\circ, +20^\circ)$ and $(-100^\circ, +30^\circ)$, and at $(+120^\circ, 0^\circ)$ and $(+120^\circ, -40^\circ)$, and is not observed in some high- φ high- θ trajectories such as $(\varphi, \theta) = (+120^\circ,$ $\pm 70^{\circ}$). Apparently the pathology is absent when the closest initial Ge35–C11 distance $d_{Ge35-C11}$ is ≥ 2.74 Å, with pathology permitted but not mandatory for 2.73 Å > $d_{Ge35-C11} \ge 2.57$ Å.

The second class of trajectory pathologies involves unwanted high-energy covalent bond formation between HAbstH and GeRad tool handles during very high- φ trajectories where the handles are computationally forced into experimentally unrealistic proximity at the start of an energy minimization. Five distinct structural rearrangements were recorded, of two general subclasses: two instances (Figs. 6(D and F)) in which a handle-cage shoulder-bond to Ge35 is broken, resulting in diradicalization of the Ge atom, and three instances (Figs. 6(B, C and E)) in which multiple rebonding events between handlecage atoms are accompanied by the release of an H₂ molecule, a likely spurious result. These rearrangements



Fig. 4. Three views of spherical representation of PES for reaction I (endoergic = blue, exoergic = red) as a function of tooltip positional angles φ and θ (see Fig. 2) expressed on the cartesian XYZ coordinate system at tooltip separation distance R = 4.85 Å and GeRad rotational angle $\rho = +40^{\circ}$. Yellow region is excluded due to handle collision.



Fig. 5. Progression of Ge35–C12 bonding reaction in Reaction I as a function of R (Å) for a fixed (φ , θ , ρ) = (+40°, +70°, +40°) approach trajectory at 0.05 Å increments. Left: C1–C11–C12 (black) and C11–C12–H28 (red) bond angles (deg). Center: Ge35–C12 (black) and C11–C12 (red) bond distances (Å). Right: PES (eV).

have not been investigated in further detail since they occur only well outside of the recommended (φ , θ) operating range of ~ ($\pm 80^{\circ}$, $\pm 80^{\circ}$) for Reaction I, and are reported here for completeness.

3.4. PES as a Function of Rotational Angle ρ

Figure 7 shows the effects of GeRad tooltip rotational angle ρ on the 1-dimensional PES for Reaction I. At (φ , θ) = (0°, 0°) for R = 4.85 Å, the PES has negligible variation with changing ρ because the HAbstH and GeRad handles are maximally distant, thus minimizing handle–handle steric interactions. Using the viable (φ , θ) = (+40°, +70°) trajectory, varying ρ has greater effect—there is a smaller variation of about ± 0.03 eV at a more distant separation distance of R = 4.85 Å and a somewhat larger variation of ± 0.14 eV as final Ge35–C12 bond formation is reached at R = 4.35 Å, with reaction energy minimized in this case at $\rho = +40^{\circ}$, $+160^{\circ}$, and $+280^{\circ}$. There are three peaks and valleys due to the threefold symmetry of the GeRad tooltip: the Ge–C bonds of the three sidewall CH₂ groups bonded to Ge35 are spaced 120° apart, as are the three gaps between those shoulder groups, producing an asymmetric steric interaction when GeRad is brought into closer proximity to the HAbstH handle and rotated to various values of ρ . At the most extreme values of $\theta = \pm 90^{\circ}$, the choice of ρ ($\sim \varphi$) has greatest effect because of the strong handle–handle interactions as GeRad rotations in ρ move tool handle sidewall CH₂ groups into and out of juxtaposition on the apposed tool handles. In particular, there is a



Fig. 6. Six instances of handle-handle rearrangements observed during experimentally unrealistic close apposition of tooltip handles for Reaction I, at R = 4.85 Å and $\rho = +40^\circ$, for (φ , θ) settings: (A) (+100°, -30°), (-100°, +30°), (-100°, +20°), (+120°, -40°), and (+120°, 0°); (B) (-110°, -10°); (C) (-120°, 0°); (D) (-120°, +20°); (E) (+150°, -40°); and (F) (-150°, -50°). (C = yellow, H = blue, Ge = white).



Fig. 7. PES for Reaction I as a function of GeRad tooltip rotational angle ρ , for trajectory (φ , θ) = (0°, 0°) at R = 4.85 Å and trajectory (φ , θ) = (+40°, +70°) at R = 4.85 Å and 4.35 Å (at left), and trajectories $\theta = \pm 90^{\circ}$ at R = 4.85 Å (at right) where φ displacements are equivalent to ρ .

variation of ± 0.38 eV depending on the choice of ρ , and with the reaction energy for Reaction I minimized at φ $(\sim \rho) = 0^{\circ}, \pm 120^{\circ}$ in this case. Note that if the GeRad tool was held fixed in space and instead the HAbstH workpiece was rotated around its central axis, we would expect to see the same trimodal pattern in net energy due to the similar threefold symmetry of the HAbstH handle structure.

Figure 7 shows that the impact of ρ on net reaction energy can sometimes be significant, especially near the perimeter of the recommended (φ , θ) operating range of $\sim (\pm 80^\circ, \pm 80^\circ)$ for Reaction I. Since the choice of ρ for which Reaction I net energy will be minimized is a function of the selected approach trajectory (φ , θ) but is not a function of *R*, Figure 8 explores the space of minimumand maximum-energy ρ values as a function of φ and θ in the two representative ($+\varphi, \pm \theta$) quadrants to 20° resolution at R = 4.85 Å. The results confirm that:

(a) the impact of ρ on net reaction energy increases with larger φ or θ (Figs. 8(A and B)) and may vary significantly depending upon trajectory (Fig. 8(D)),

(b) the increase in net reaction energy caused by choosing the most detrimental versus the most optimal ρ ranges from 0.0 eV to +0.7 eV (Fig. 8(B)), and

(c) the choice of optimal ρ (Fig. 8(C)) can vary from 0° to 100° depending upon choice of (φ , θ).

The apparent patternlessness of optimal ρ settings in Figure 8(C) is partly due to the occurrence in some cases of multiple minima having small energy differences within the computational error and partly artifactual due to wraparound (i.e., $\rho = 0^\circ = 120^\circ$).

For trajectories where the most optimal and most detrimental ρ values give reaction energies that differ only slightly (i.e., white areas in Fig. 8(B)), the precise value of ρ is inconsequential in determining reaction reliability and thus the ability to positionally control ρ during the experiment may not be crucial. For other trajectories where this energy differential is large (i.e., dark blue areas in Fig. 8(B)), ρ can be a significant factor in determining reaction reliability in which case the ability to positionally control ρ during the experiment would be very important.

3.5. Lateral Displacement Error Tolerance

To specify a useful experimental protocol it is also necessary to determine the maximum tolerable lateral misplacement error of GeRad that will still result in a successful consummation of Reaction I. We start by defining the U-axis as a vector pointing from O'' to C34 and the V-axis as a vector originating at O" and perpendicular to U that points parallel and codirectional with a vector from C30 to C32 (Fig. 9). We can then examine whether the Ge35-C12 bond still forms when GeRad is translationally displaced within the UV plane away from its intended position at any point within a particular approach trajectory. A comprehensive analysis of all possible displacements from every point along all possible approach trajectories is beyond the scope of this paper, so we analyzed a representative reaction point (R = 4.35 Å) along a single exemplar approach trajectory: $(\varphi, \theta, \rho) =$ $(+40^\circ, +70^\circ, +50^\circ)$. The lateral displacement of GeRad from its intended trajectory is reported as a displacement angle δ measured from U and a displacement radial distance Δr measured from O".

Simulations began by examining small Δr , moving to larger Δr , simulating progressively larger displacement error circles. At some Δr we would expect to find that Ge35 and C12 are too far apart to form the desired bond. However, before that point is reached a competing Ge35-C11 bonding pathology is encountered, initially only at $\delta = 90^{\circ}$ where the GeRad error displacement moves Ge35 exactly in the C11 direction. This $\delta = 90^{\circ}$ pathology is observed at $\Delta r = 0.6$ Å but not at $\Delta r =$ 0.5 Å. Thus the maximum tolerable GeRad tooltip displacement error for successfully completing Reaction I along the exemplar trajectory at $\delta = 90^\circ$ is 0.5 Å. With increasing Δr beyond 0.6 Å, the range of δ over which the Ge35-C11 bonding pathology occurs increases-e.g., by $\Delta r = 1.0$ Å the pathology is found over $\delta = 50^{\circ} - 130^{\circ}$ although the desired Ge35-C12 bonding is still obtained at all other δ ; at $\Delta r = 1.5$ Å, Ge35–C12 bonding is obtained only at $\delta = 180^{\circ}$; and at $\Delta r = 1.6$ Å the desired Ge35–C12

REVIEW



Fig. 8. Effects on reaction energy for various choices of GeRad tooltip rotational angle ρ as a function of (φ, θ) trajectory for R = 4.85 Å in Reaction I: (A) minimum net energy E_{\min} (eV) produced by choosing the optimum ρ value for each trajectory; (B) increase in net reaction energy (eV) over minimum (E_{\min}) produced by choosing the most detrimental ρ value that yields the highest reaction energy E_{\max} , or $|E_{\max}-E_{\min}|$; (C) choice of optimum ρ value (deg) that produces the minimum net energy shown in (A) for each trajectory; and (D) energy variations as a function of ρ for trajectories (φ, θ) = (+80°, +60°), (0°, +60°) and (+60°, +40°). Charts (A)–(C): *E* or $\Delta E < 0$ (red), = 0 (white), > 0(blue); optimum ρ angles in yellow; excluded data points in gray.

bonding cannot be obtained at any δ (tested full circle at 20° increments). These results are broadly consistent with similar results from previous analyses of tolerable mispositioning errors reported elsewhere.^{19, 26}

3.6. Optimal Tooltip Trajectories

3.6.1. Single-Setting Optimal Trajectories

Perhaps the simplest method for selecting an optimal approach trajectory for Reaction I is to choose a single (φ, θ) trajectory that continuously maintains an acceptably low net reaction energy throughout the entire approach, starting from infinite separation between tool and workpiece and concluding with Ge35–C12 bond formation at R = 4.35 Å. The objective is to allow tool and workpiece to be positioned in the energy landscape on a valley floor of acceptable depth but maximum width which

will permit successful consummation of Reaction I even in situations where tooltip placement error may be significant, e.g., the (φ , θ , ρ) = (+40°, +70°, +40°) approach trajectory described in Section 3.2 (Fig. 5). This method provides a safe and adequate approach trajectory that minimizes demands on the reliability of an experimental positional control system, since the controls can be set once at the start of the reaction and held constant through its conclusion.

A more systematic method for generating a general range of workable single-setting trajectories starts with the two PES charts for R = 4.85 Å and R = 4.35 Å from Figure 3, which represent the "before" and "after" cases of H28 and C11–C12 movement during tooltip approach the key mechanical events of Reaction I. The intersection of all exoergic points simultaneously present on both PES surfaces yields a large subset of acceptable approach trajectories (Fig. 10). The 10 best (φ , θ) trajectories (as



Fig. 9. Geometry used for displacement error tolerance, with HAbstH shown in foreground and GeRad shown in background in position to consummate Reaction I; Δr and δ are defined as the radial and angular displacement of the GeRad tool relative to an exemplar (φ , θ , ρ) = (+40°, +70°, +50°) approach trajectory, shown displaced up and to the right towards 1 o'clock in the drawing. (C = yellow, H = blue, Ge = white).

indicated) have net energies within 0.01 eV of the global minimum. An experimentalist can be reasonably confident that any trajectory selected from within the annular distribution of (φ , θ) points (after adjusting for proper ρ ; see Fig. 8) should enable Reaction I to successfully proceed.

3.6.2. Compound Optimal Trajectories

It is also possible to construct a specific compound optimal trajectory comprised of two or more single-setting trajectories that continuously maintains the lowest possible net reaction energy at every separation distance, starting from infinite separation between tool and workpiece and concluding with Ge35–C12 bond formation at R =4.35 Å. This method maximizes the probability of a correct reaction based on energetics, but assumes that tooltip



Fig. 10. Single-trajectory analysis from Boolean intersection of R = 4.85 Å and R = 4.35 Å PES excergic (red) zones, for $\rho = +40^{\circ}$ in Reaction I. Trajectories within ~0.01 eV of global minimum are solid dots.

placement error is small enough to allow hopping between designated neighboring PES surfaces (a significant challenge, experimentally). In this method, during each 0.05 Å step in *R* the experimentalist is permitted to alter one or both of the φ or θ settings by at most one increment of minimum resolution ($\Delta = 10^{\circ}$ in either φ or θ for this study) to ensure smooth and continuous motion, shifting the tool from one (φ , θ) trajectory to another immediately adjacent ($\varphi \pm \Delta$, $\theta \pm \Delta$) trajectory in order to maintain minimum energy at each step. Future studies could employ a smaller Δ to provide an even smoother compound trajectory.

To construct our representative optimized compound trajectory, we start by recomputing absolute energy minima for (φ, θ, ρ) to 10° resolution at both R = 4.85 Å and R = 4.35 Å, obtaining the following results after one iteration: For R = 4.85 Å, $(\varphi, \theta, \rho) = (+50^\circ, +70^\circ)$, +20°), $E_{\min} = -0.508$ eV; and $(\varphi, \theta, \rho) = (-50^\circ, +70^\circ,$ +60°), $E_{\min} = -0.505$ eV. For R = 4.35 Å, $(\varphi, \theta, \rho) =$ $(+30^{\circ}, +10^{\circ}, +90^{\circ}), E_{\min} = -0.504 \text{ eV}; \text{ and } (\varphi, \theta, \rho) =$ $(-20^{\circ}, +30^{\circ}, +110^{\circ}), E_{\min} = -0.504$ eV. In each case, an optimum ρ (yielding lowest energy) was determined from a fixed (φ, θ) , after which the new ρ was held fixed and (φ, θ) was reoptimized. The first iteration produced only minor -0.002 eV/-0.001 eV (*R* = 4.85 Å) and -0.045 eV/-0.009 eV (R = 4.35 Å) improvements in minimum energy, though a more thorough (computationally expensive) analysis might iterate until zero change in minimum energy was attained. Trajectory charts (E vs. R) for constant (φ, θ, ρ) in all four cases (Fig. 11(A)) reveal larger barrier heights for the R = 4.35 Å trajectories, so we choose $(\varphi, \theta, \rho) = (+50^{\circ}, +70^{\circ}, +20^{\circ})$ at R = 4.85 Å (which also has the lowest E_{\min} of the four choices) as the starting point for our representative optimized compound trajectory.

Starting from this base trajectory, E versus R charts are computed for a bracketing 3×3 grid of nearest-neighbor (φ, θ) trajectories in $\pm 10^{\circ}$ increments (Fig. 11(B)). For example, the (φ, θ) trajectory yielding the lowest energy at R = 4.85 Å + 0.05 Å = 4.90 Å is selected as the next point in the compound trajectory. The process is iterated in 0.05 Å increments outward to R = 5.90 Å and inward to R =4.35 Å, yielding the representative locally optimized compound trajectory shown in Figure 11(C) (data in Table II). In the present work, ρ was held constant at +20° for computational convenience; a more thorough (computationally expensive) analysis would reoptimize (φ, θ, ρ) at every step to find the best ρ . Calculating a globally optimized compound trajectory would require calculating all possible E versus R curves to create a comprehensive collection from which the absolute energy-minimized trajectory could definitively be assembled to whatever resolution was required. Trajectory analysis software could be developed to calculate the optimum compound trajectory automatically. However, it is not clear that optimized compound

REVIEW



REVIEW

Fig. 11. Construction of a representative locally optimized compound trajectory for Reaction I: (A) Four ρ -optimized (φ , θ , ρ) trajectories exhibiting minimum net reaction energy at R = 4.85 Å ((+50°, +70°, +20°) and (-50°, +70°, +60°)) and at R = 4.35 Å ((+30°, +10°, +90°) and (-20°, +30°, +110°)); (B) nearest-neighbor trajectories to (φ , θ) = (+50°, +70°) at ρ = +20° and R = 4.85 Å; and (C) a locally optimized low-barrier compound GeRad tooltip approach trajectory for ρ = +20° and allowing ≤10° angle changes at each 0.05 Å step (see Table II).

trajectories represent a sufficient improvement over wellchosen single-setting trajectories to justify their additional computational and experimental complexities.

3.6.3. Low-Barrier Optimal Trajectories

Another important criterion for successful completion of a positionally controlled mechanosynthetic reaction is the minimization of energy barriers. If the activation energy for a selected approach trajectory is too high, the tools may not be able to deliver sufficient force to compel the reaction to go forward, or the tool or workpiece might suffer unacceptably large flexures during their attempt to overcome a high barrier, potentially opening the door to additional trajectory or reaction pathologies. For example, the highest reaction barrier within the recommended (φ , θ) operating range of ~ ($\pm 80^\circ$, $\pm 80^\circ$) for Reaction I ($\Delta E \sim +0.48 \text{ eV}$) occurs near (φ , θ , ρ) = (0° , 0° , $+40^\circ$) (Fig. 12).

An energy barrier map for two representative $(+\varphi, \pm\theta)$ quadrants of the (φ, θ) space at fixed $\rho = 50^{\circ}$, comprised of a uniform distribution of 102 data points at 10° intervals in the range $\varphi = +30^{\circ}$ to $+80^{\circ}$ and $\theta = -80^{\circ}$ to $+80^{\circ}$, shows the maximum endoergicity encountered along each

R (Å)	arphi	θ	E (eV)	R (Å)	arphi	θ	E (eV)	R (Å)	arphi	θ	<i>E</i> (eV)
5.90	+40°	+60°	+0.041	5.35	+60°	+70°	-0.134	4.80	+50°	+70°	-0.507
5.85	$+40^{\circ}$	$+60^{\circ}$	+0.046	5.30	$+50^{\circ}$	$+80^{\circ}$	-0.453	4.75	$+40^{\circ}$	$+70^{\circ}$	-0.506
5.80	$+50^{\circ}$	$+60^{\circ}$	+0.052	5.25	$+50^{\circ}$	$+80^{\circ}$	-0.468	4.70	$+40^{\circ}$	$+70^{\circ}$	-0.503
5.75	$+40^{\circ}$	$+60^{\circ}$	+0.058	5.20	$+50^{\circ}$	$+80^{\circ}$	-0.480	4.65	$+50^{\circ}$	$+60^{\circ}$	-0.500
5.70	$+40^{\circ}$	$+60^{\circ}$	+0.065	5.15	$+50^{\circ}$	$+80^{\circ}$	-0.488	4.60	$+50^{\circ}$	$+60^{\circ}$	-0.497
5.65	$+40^{\circ}$	$+60^{\circ}$	+0.072	5.10	$+40^{\circ}$	$+80^{\circ}$	-0.493	4.55	$+40^{\circ}$	$+60^{\circ}$	-0.491
5.60	$+40^{\circ}$	$+60^{\circ}$	+0.079	5.05	$+40^{\circ}$	$+80^{\circ}$	-0.498	4.50	$+40^{\circ}$	$+60^{\circ}$	-0.487
5.55	$+40^{\circ}$	$+60^{\circ}$	+0.087	5.00	$+40^{\circ}$	$+80^{\circ}$	-0.500	4.45	$+40^{\circ}$	$+60^{\circ}$	-0.479
5.50	$+40^{\circ}$	$+60^{\circ}$	+0.096	4.95	$+50^{\circ}$	$+70^{\circ}$	-0.500	4.40	$+40^{\circ}$	$+60^{\circ}$	-0.469
5.45	$+50^{\circ}$	$+60^{\circ}$	+0.110	4.90	$+50^{\circ}$	$+70^{\circ}$	-0.505	4.35	$+40^{\circ}$	$+60^{\circ}$	-0.456
5.40	$+50^{\circ}$	+70°	+0.112	4.85	$+50^{\circ}$	$+70^{\circ}$	-0.508				

Table II. Representative locally-optimized compound trajectory for Reaction I, with $\rho = +20^{\circ}$ and allowing $\leq 10^{\circ}$ angle changes at each 0.05 Å step.

REVIEW

approach trajectory (Fig. 13). The peak energy barriers occur at a variety of separation distances *R* (not shown), and range from a minimum of +0.102 eV at (φ , θ) = (+50°, +60°) to a high of +0.30 eV at (φ , θ) = (+30°, 0°) approaching the "hydrogen hill" at the leftmost edge of the chart, with the maximum barrier of +0.48 eV at (φ , θ) = (0°, 0°) not directly visible on the chart. The single-setting (φ , θ , ρ) = (+50°, +70°, +20°) approach trajectory lies in a favorable region of the energy barrier map, and other optimal trajectories computed using methods described in Sections 3.6.1 and 3.6.2 might be enhanced by selecting neighboring paths possessing reduced barrier heights.

The barrier-driven flexure through an angle α of the tip of the C–C≡C group away from linear configuration as the GeRad tooltip approaches C12 can be crudely estimated from the standard bond-bending term in molecular mechanics: $E_{\text{bend}} = 1/2k_{\text{bend}} (\alpha - \alpha_{\text{eq}})^2 (1 + k_{\text{sextic}} (\alpha - \alpha_{\text{eq}})^4)$, where k_{bend} is the angle-bending force constant, α_{eq} is the equilibrium bond angle, and $k_{\text{sextic}} = 0.754 \text{ rad}^{-4}$ for C–C bonds in MM2. Data from a published⁸ bending potential chart for the adamantane-handled (C₉H₁₅)C–C≡C system (the HAbst tooltip) gives $k_{\text{bend}} \sim 370 \text{ zJ/rad}^2$, hence surmounting a ~0.14 eV barrier on the (φ , θ , ρ) = (+50°, +70°, +20°) approach trajectory should produce a maximum flexure (immediately prior to Ge35–C12 bond formation) of $\alpha \sim 20^\circ$, or ~0.9 Å deflection at the end of a 2.66 Å C–C≡C lever arm requiring a very modest 0.25 nN of mechanical force to overcome. This estimate



Fig. 12. PES for Reaction I as a function of tooltip separation distances *R* using the highest-barrier ($\Delta E \sim +0.48 \text{ eV}$) approach trajectory at (φ , θ , ρ) = (0°, 0°, +40°).

is consistent with the ~0.4 Å prebonding ethynyl repulsion displacement computationally predicted for the O"-C12 distance as GeRad approaches (shaded area, Fig. 14), given that no prebonding compression is evident in O"-Ge35 but that some portion of the total compression energy is likely partitioned into each of the two tools.

3.6.4. Other Optimal Trajectories

Figure 8(B) indicates another possible optimal trajectory criterion—minimum ρ angle impact on net reaction energy—that yields specific approach trajectories at R = 4.85 Å such as (φ , θ) = (+80°, 0°) which is both very exoergic and maximally insensitive to ρ angle setting, perhaps



Fig. 13. Energy barrier map for Reaction I (endoergic = blue, exoergic = red, energy in eV) as a function of tooltip positional angles φ and θ . Minimum barrier height occurs at various tooltip separation distances *R* depending on value of φ and θ , taking GeRad rotational angle $\rho = +50^{\circ}$, with lowest energy value +0.102 eV at (φ , θ) = (+50°, +60°) where the guidelines intersect.



Fig. 14. Deflection of C12 at ethynyl tip of HAbstH and partial extrusion of Ge35 during Ge35–C12 bonding event along (φ , θ , ρ) = (+50°, +70°, +20°) approach trajectory in Reaction I, as GeRad travels from R = 6.60 Å to 4.35 Å.

ideal in situations where the experimentalist finds ρ difficult or impossible to control. Other specialized trajectory criteria may be investigated in future work.

4. REACTION II: ABSTRACT APICAL H FROM HAbstH USING GeRad2 TOOL

In Reaction II of the HAbst recharge reaction sequence RS5 (Fig. 1), a second GeRad tool ("GeRad2") is brought up to the transactional hydrogen atom (H28), and at some separation distance H28 jumps to the incoming GeRad2 tool, having been abstracted away from the tip of the HAbstH tool. This allows the C11-C12 bond order to increase from 2 to 3, causing the carbon dimer to seek to resume linearity relative to the adamantane central axis, and eliminates the open radical site on the carbon atom proximal to the HAbstH base structure that was created during Reaction I. The hydrogenated GeRad2-H tool may then be withdrawn from the system along any noncollisional trajectory, the choice of which is noncritical (and is not examined further in the present work) because there are no remaining open radicals in the system and so all tooltips are in an inert condition. The GeRad2-H tooltip is subsequently restored to an active GeRad2 tooltip using a separate recharge reaction sequence⁷ specific to that tool, e.g., contacting the GeRad2-H to a depassivated flat bulk diamond surface, causing the H to donate to the surface.

After defining the tooltip geometry and coordinate system for Reaction II (Section 4.1) we calculate the reaction PES (potential energy surface) as a function of positional angles $\varphi_{\rm H}$ and $\theta_{\rm H}$ (Section 4.2), describe the trajectoryrelated pathologies (Section 4.3), calculate the reaction PES as a function of rotational angle $\rho_{\rm H}$ of the incoming GeRad2 tool (Section 4.4), estimate the tolerance for lateral displacement error in tooltip positioning for Reaction II (Section 4.5), then recommend some optimal GeRad2 tooltip trajectories for this reaction (Section 4.6).

4.1. Tooltip Geometry and Coordinate System

A positionally unconstrained single-cage-handle HAbstH-GeRad complex (as created in Reaction I) has two stable minimum-energy configurations-a "cis" form with the H28 atom and the radical site on the same side of the ethynyl C=C dimer, and a "trans" form with H28 and the radical site on opposite sides of the C \equiv C dimer (Fig. 15). We confirm earlier work⁷ reporting that the unconstrained "trans" form is -0.12 eV lower in energy than the unconstrained "cis" form. However, in a mechanosynthetic apparatus the two handles comprising this structure are not unconstrained, but rather are continuously positionally controlled. Using positional control, a mechanical barrier can be imposed that forces the structure to adopt or to retain either configuration since both are stable stationary states with no imaginary frequencies. In the present work, as in previous work,⁷ we presume that positional control is employed to establish and maintain the system in the slightly higher energy "cis" state because this configuration provides greater steric accessibility to H28 by the incoming GeRad2 tooltip.

We start by assuming that the displacement distance R producing the lowest energy on the optimal trajectory represents the endpoint of Reaction I, and hence constitutes the starting point for Reaction II. Hence the tooltip geometry and coordinate system for Reaction II is based on the minimum energy configuration for HAbstH-GeRad in "cis" geometry at $(\varphi, \theta, \rho) = (+50^\circ, +70^\circ, +20^\circ)$ and R = 4.85 Å (Fig. 16). Structural data for this initial geometry are as follows: A(C1-C11-C12) = +151.059 deg,C1-C11-C12-H28 dihedral = +179.775 deg, A(Ge35-C12-C11) = +129.257 deg, A(Ge35-C12-H28) = +112.258 deg, and R(Ge35-C12) = 1.984 Å. The first coordinate origin O_H is defined as the equilibrium starting position of H28 with GeRad2 removed to infinite distance. The positive $X_{\rm H}$ axis originates at $O_{\rm H}$ and points in the direction from the starting position of C12 to O_H. The



Fig. 15. Unconstrained single-cage-handle HAbstH-GeRad structure at Reaction I completion has two stable minimum-energy configurations. (C = yellow, H = blue, Ge = white).

 $Y_{\rm H}$ axis originates at $O_{\rm H}$, lies perpendicular to the $X_{\rm H}$ axis and in the plane containing the starting positions of atoms C1, C11, C12 and Ge35, and points away from the GeRad tooltip containing Ge35. The $Z_{\rm H}$ axis also originates at $O_{\rm H}$ and lies perpendicular to $X_{\rm H}$ and $Y_{\rm H}$ axes following the right-hand rule. The approaching GeRad2 tool is initially oriented relative to the HAbstH-GeRad workpiece such that a line extending backwards through $O_{\rm H}$ and Ge65 perpendicularly penetrates the plane defined by the 3 fixed GeRad2 tool base carbon atoms (C59, C66, and C74), intersecting a second origin $O'_{\rm H}$ which lies in the C59/C66/C74 plane and is equidistant from C59, C66 and C74, analogous to origins O and O''.

In this spherical coordinate system, $\varphi_{\rm H}$ is defined as the angle from the $X_{\rm H}$ axis to the $Y_{\rm H}$ axis of the projection of the vector pointing from O_H to O'_H onto the $X_H Y_H$ plane. Note that $+\varphi_{\rm H}$ is defined as rotation toward the $-Y_{\rm H}$ axis in the arrow direction for consistency with prior usage in Reaction I. $\theta_{\rm H}$ is defined as the angle from the $X_{\rm H}Y_{\rm H}$ plane to the vector pointing from O_H to O'_H , with $-90^\circ \le \theta_H \le$ $+90^{\circ}$ and $-180^{\circ} \le \varphi_{\rm H} \le +180^{\circ}$. Radial distance $R_{\rm H}$ is defined as the distance between origins O_H and O'_H . The rotational state of HAbstH-GeRad is completely specified by $(\varphi, \theta, \rho) = (+50^\circ, +70^\circ, +20^\circ)$. The rotational state of GeRad2, specified by $\rho_{\rm H}$, is measured as the angle taken from the $O'_{\rm H}$ -to-C59 vector to the $Y_{\rm H}$ -axis vector when GeRad2 is virtually repositioned to $(\varphi_{\rm H}, \theta_{\rm H}) = (0^{\circ}, 0^{\circ})$ placing both $O'_{\rm H}$ and Ge65 on the $X_{\rm H}$ axis, with $+\rho_{\rm H}$ taken in the counterclockwise direction as viewed from O'_H looking toward O_{H} . Thus, rotation to $+\varphi_{H}$ becomes equivalent to rotation to $-\rho_{\rm H}$ at $\theta_{\rm H} = +90^{\circ}$, or to $+\rho_{\rm H}$ at $\theta_{\rm H} = -90^{\circ}$, consistent with prior usage in Reaction I. The positioning of GeRad2 is controlled by constraining atoms C59, C66, and C74 in the GeRad2 handle base.

4.2. PES as a Function of Positional Angles $\varphi_{\rm H}$ and $\theta_{\rm H}$

Since well-separated HAbstH-GeRad and GeRad2 each have one unpaired electron, the system of workpiece + tooltip can have singlet or triplet multiplicity. The PES as a function of workpiece-tooltip separation distance $R_{\rm H}$ for the ideal ($\varphi_{\rm H}$, $\theta_{\rm H}$, $\rho_{\rm H}$) = (0°, 0°, 0°) approach trajectory (Fig. 17) shows that the system remains in the unbonded lower-energy triplet state down to $R_{\rm H}$ = 5.90 Å (with Ge65 roughly 3.05 Å away from H28), but at $R_{\rm H}$ = 5.80 Å (or closer) the singlet state has lower energy and the Ge65– H28 bond has formed, indicating a successful abstraction of the hydrogen atom. Figure 17 indicates that the abstraction reaction may be barrierless, consistent with similar results previously reported elsewhere.^{7,8}

The PES for the Ge65-H28 abstraction reaction as a function of positional angles $\varphi_{\rm H}$ and $\theta_{\rm H}$ is shown in Figure 18 for displacement distance $R_{\rm H} = 5.80$ Å and $\rho_{\rm H} = 0^{\circ}$, compiled from a total of 343 underlying data points at 10° intervals. The PES is uniformly flat and highly excergic across a $\pm 40^{\circ} \times \pm 80^{\circ}$ region centered on $(\varphi_{\rm H}, \theta_{\rm H}) = (0^{\circ}, 0^{\circ})$, with net reaction energies approximating -1.50 eV over most of this space but rising no higher than -0.75 eV even at the periphery. (The computed absolute minimum energy of -1.576 eV actually occurs at $(\varphi_{\rm H}, \theta_{\rm H}) = (0^{\circ}, +10^{\circ})$ but this is only -0.004 eV below the value at the assumed ideal $(\varphi_{\rm H}, \theta_{\rm H}) = (0^{\circ}, 0^{\circ})$ setting, well below the accuracy of the computational method used.) High endoergic mountains are beginning to appear at $\varphi_H \geq +50^\circ$ on the right side of the chart (approaching Ge35) and also at $\varphi_{\rm H} \leq -90^{\circ}$ on the left side of the chart (approaching C11-C1) due to rapidly rising steric repulsion between closely proximated HAbstH-GeRad and



Fig. 16. Coordinate systems for Reaction II: Positionally controlled reactant tooltips prior to reaction, defining $ph_{H}(\varphi_{H})$ and $theta_{H}(\theta_{H})$ (top image), and definition of tooltip axial rotation angle $rho_{H}(\rho_{H})$ (bottom image). (C = yellow, H = blue, Ge = white).



Fig. 17. Singlet and triplet PES as a function of $R_{\rm H}$ for the ideal ($\varphi_{\rm H}$, $\theta_{\rm H}$, $\rho_{\rm H}$) = (0°, 0°, 0°) approach trajectory for Reaction II.



Fig. 18. Singlet PES for Reaction II (endoergic = blue, exoergic = red, excluded = gray) at tooltip separation distance $R_{\rm H} = 5.80$ Å for approach trajectories in the range ($\varphi_{\rm H}, \theta_{\rm H}, \rho_{\rm H}$) = (±180°, ±90°, 0°).

GeRad2 tool handles at those high angles. Spherical representations of the smoothed PES (Fig. 19) show regions of favorable (exoergic) and unfavorable (endoergic) net reaction energies from the viewpoint of a GeRad2 tool as it approaches the H28 atom on the HAbstH-GeRad complex, with two yellow regions excluded due to handle collisions on either side. Note that the PES is expected to be slightly asymmetrical between $+\theta_{\rm H}$ and $-\theta_{\rm H}$ hemispheres because GeRad is rotated to $\rho = +20^{\circ}$ in the HAbstH-GeRad complex, causing that complex to lie asymmetrically across the $X_{\rm H}Y_{\rm H}$ plane.

4.3. Trajectory Pathologies of Reaction II

The first trajectory pathology of Reaction II occurs along a few mid-range $-\varphi_{\rm H}$ trajectories that allow the Ge65 radical site to pass too close to C11 as GeRad2 approaches H28, enabling the unwanted bonding of Ge65 and C11 (Fig. 20) in preference to the desired Ge65–H28 bonding to achieve a successful abstraction. On the $-\varphi_{\rm H}$ side of the recommended ($\varphi_{\rm H}, \theta_{\rm H}$) operating range of $\sim (\pm 40^{\circ}, \pm 80^{\circ})$ for the normal abstraction reaction, there is a second lowenergy valley about 20° wide in $\varphi_{\rm H}$ where the Ge65–C11 pathology occurs, visible on the PES in Figure 18, in the range $(\varphi_{\rm H}, \theta_{\rm H}) = (-60^{\circ} \text{ to } -80^{\circ}, \pm 80^{\circ})$. Interestingly, the Ge65–C11 pathology also occurs in the entire range ($\varphi_{\rm H}$, $\theta_{\rm H}) = (-90^{\circ}, -80^{\circ} \text{ to } +70^{\circ})$, but only the trajectories at $\theta_{\rm H} = -60^{\circ}$ to -80° and $+50^{\circ}$ to $+70^{\circ}$ are overall excergic at $R_{\rm H} = 5.80$ Å. The other trajectories are endoergic overall, but the Ge65-C11 bond forms anyway because the bonded structure has lower energy (net exoergic) than the unbonded structure, since at these angles the tools have been forced into close proximity and fixed in a position where steric repulsion between handles is high. The Ge65-C11 pathology also occurs in a similar mixed-energy fashion at $\varphi_{\rm H} = -100^{\circ}$ in the ranges $\theta_{\rm H} = -50^{\circ}$ to -80° and $+50^{\circ}$ to $+80^{\circ}$, but only the $\theta_{\rm H} = -50^{\circ}$, -60° and -80° trajectories are exoergic at $R_{\rm H} = 5.80$ Å. The extent of the Ge65–C11 pathology at trajectories with $\varphi_{\rm H} < -100^{\circ}$ has not been further investigated in the present work because



Fig. 20. Crossbonding Ge65–C11 trajectory pathology observed during close apposition of tooltip handles for Reaction II at $R_{\rm H} = 5.80$ Å and $\rho_{\rm H} = 0^{\circ}$. (C = yellow, H = blue, Ge = white).

these trajectories, while of general theoretical interest, are not relevant to defining an experimental protocol involving the recommended ($\varphi_{\rm H}$, $\theta_{\rm H}$) operating range of ~ (±40°, ±80°) for Reaction II. The above examples all assume $\rho_{\rm H} = 0^{\circ}$.

A question arises as to whether a narrow low-positiveenergy barrier separates the two valleys in the range ($\varphi_{\rm H}$, $\theta_{\rm H}$, $\rho_{\rm H}$) = (-50°, -60° to +50°, 0°), as is visible in Figures 18 and 19 as a thin blue vertical reef. Stepping across the putative barrier in $\Delta \varphi_{\rm H} = 1^{\circ}$ increments along successive ($\varphi_{\rm H}$, $\theta_{\rm H}$, $\rho_{\rm H}$) = (-40° to -71°, 0°, 0°) approach trajectories at $R_{\rm H} = 5.80$ Å (Fig. 21) to improve resolution of this feature reveals a flat exoergic net reaction energy near -1.52 eV through $\varphi_{\rm H} = -45^{\circ}$, followed at $\varphi_{\rm H} =$ -46° by singlet energy jumping to a highly endoergic



Fig. 19. Three views of spherical representation of smoothed singlet PES for Reaction II (endoergic = blue, exoergic = red) as a function of tooltip positional angles $\varphi_{\rm H}$ and $\theta_{\rm H}$ expressed on the Cartesian $X_{\rm H}Y_{\rm H}Z_{\rm H}$ coordinate system at tooltip separation distance $R_{\rm H} = 5.80$ Å and GeRad2 rotational angle $\rho_{\rm H} = 0^{\circ}$. The HAbstH-GeRad complex is represented by a hydrogenated ethynyl (CCH) group attached to the Ge35 atom of GeRad. The yellow region is excluded due to handle collision.

REVIEW



Fig. 21. Singlet and triplet PES as a function of $\varphi_{\rm H}$ for a ($\theta_{\rm H}$, $\rho_{\rm H}$) = (0°, 0°) approach trajectory at $R_{\rm H} = 5.80$ Å for Reaction II (left ordinate), and Ge65–C11 distance (right ordinate), for $-71^{\circ} \le \varphi_{\rm H} \le -40^{\circ}$ in the singlet case; singlet $\rho_{\rm H} = 45^{\circ}$ approach trajectory is also shown.

+0.55 eV, well above the +0.01 eV for triplet, coinciding with failure of the normal Ge65-H28 abstraction reaction. Singlet energy again retreats below triplet only at $\varphi_{\rm H} \leq -54^{\circ}$, indicating the potential onset of Ge65–C11 pathological bonding as previously discussed: in the singlet mode, significant prebonding movement of atoms Ge65 and C11 occurs at $\varphi_{\rm H} = -46^{\circ}$, but their interatomic separation stays well above the equilibrium Ge-C bond length (according to MM2 parameter set)²⁷ of $r_0 = 1.95$ Å until $\varphi_{\rm H} \sim -61^{\circ}$ when the separation falls to ~2.32 Å, the approximate maximum length of a stretched Ge-C bond-and below which distance a stable Ge65-C11 bond can be said to have formed via an apparently barrierless radical-radical coupling misreaction. (Calculating the Morse parameter $\beta = (k_s/2D_e)^{1/2} = 1.86 \times 10^{10} \text{ m}^{-1}$ by taking Ge–C bond stiffness²⁷ $k_s = 270$ N/m and Ge–C potential well depth²⁸ $D_e = 2.44 \text{ eV}$, a Ge–C bond becomes mechanically unstable⁵ when stretched past the inflection point at $r = r_0 + \ln(2)/\beta = 2.32$ Å.) However, the system must lie in the near-equiergic triplet state between $\varphi_{\rm H} = -46^{\circ}$ to -53° because the singlet energy is much higher, hence there is apparently no significant energy barrier blocking entrance to the Ge65–C11 pathology from this direction. Rotating the incoming tool to $\rho_{\rm H} = 45^{\circ}$ does not significantly alter the endoergic "reef" structure.

Minor features evident in the second valley visible in Figure 18 are mostly attributable to the atomic granularity of approaching handle atoms. For example, at ($\varphi_{\rm H}$, $\theta_{\rm H}$, $\rho_{\rm H}$) = (-80°, -30°, 0°) atom C55 on the GeRad2 handle is forced to within 2.59 Å of atom C8 on the HAbst handle, producing a large endoergicity for the Ge65–C11 pathology, whereas at ($\varphi_{\rm H}$, $\theta_{\rm H}$, $\rho_{\rm H}$) = (-80°, +30°, 0°) handle atoms C55 and C8 remain 3.45 Å apart, yielding an exoergic Ge65–C11 pathology.

A second possible trajectory pathology of Reaction II was predicted for the $\theta_{\rm H} = -90^{\circ}$ case in which structure optimization in the singlet state leads to partial Ge65-Ge35 bonding (Fig. 22) with a computed separation distance of ~ 2.77 Å (vs. ~ 3.93 Å in the triplet state). This would represent a highly stretched but fully formed Ge-Ge bond, since the Morse parameter $\beta = (k_s/2D_s)^{1/2} =$ $1.6 \times 10^{10} \text{ m}^{-1}$ taking Ge–Ge bond stiffness $k_s \sim 160 \text{ N/m}$ (est.)²⁷ and Ge–C potential well depth $D_e = 1.95 \text{ eV}$,²⁹ then $r = r_0 + \ln(2)/\beta = 2.84$ Å given an equilibrium Ge–Ge bond length of $r_0 = 2.41$ Å.²⁹ While typical singlet reaction energies are about +0.3 eV (slightly endoergic) and triplet energies are lower, the competing desired Ge65-H28 abstraction reaction apparently fails to occur in these cases. These results may be artifactual due to failure of the optimization algorithm to locate the actual minimum of the



Fig. 22. Possible Ge65–Ge35 bonding pathology observed for trajectory ($\varphi_{\rm H}$, $\theta_{\rm H}$, $\rho_{\rm H}$) = (+90°, -90°, 0°) at $R_{\rm H}$ = 5.80 Å for Reaction II. (C = yellow, H = blue, Ge = white).

REVIEW

H28 abstraction reaction so that the optimization falls into a local minimum. Further details of this possible pathology have not been investigated in the present work because these trajectories lie outside the recommended ($\varphi_{\rm H}$, $\theta_{\rm H}$) operating range of ~ (±40°, ±80°) for Reaction II.

A third class of trajectory pathologies involving unwanted high-energy covalent bond formation between HAbstH-GeRad and GeRad2 tool handles during trajectories involving close handle–handle proximity is possible but was not investigated in the present work because these trajectories also lie well outside the recommended ($\varphi_{\rm H}$, $\theta_{\rm H}$) operating range of ~ (±40°, ±80°) for Reaction II.

4.4. PES as a Function of Rotational Angle $\rho_{\rm H}$

Figure 23 shows the effects of GeRad2 tooltip rotational angle $\rho_{\rm H}$ on the 1-dimensional PES for Reaction II. At $(\varphi_{\rm H}, \theta_{\rm H}) = (0^{\circ}, 0^{\circ})$ for $R_{\rm H} = 5.80$ Å, the PES has negligible variation (0.0042 eV) with changing $\rho_{\rm H}$ and there is no apparent effect on this PES if $|\theta_{\rm H}|$ is increased to 60° at $\varphi_{\rm H} = 0^{\circ}, +30^{\circ}, \text{ or } -30^{\circ}$. Due to the threefold symmetry of the GeRad2 tooltip, there are three critical values for $\rho_{\rm H}$ (0°, 120° and 240°) that produce minimum net reaction energy. These critical values, as well as the shape of the PES, apparently do not vary significantly with $\theta_{\rm H}$ at workable values of $\varphi_{\rm H}$. Within the recommended ($\varphi_{\rm H}, \theta_{\rm H}$) range of $\sim (\pm 40^\circ, \pm 80^\circ)$ for Reaction II, the variation in new reaction energy as a function of ho_{H} increases very slowly with $\varphi_{\rm H}$, reaching only $\Delta E_{\rho\rm H} = 0.20$ eV by ($\varphi_{\rm H}$, $\theta_{\rm H}$) = (+30°, 0°), 0.005 eV by ($\varphi_{\rm H}$, $\theta_{\rm H}$) = (+30°, +60°), and 0.032 eV by $(\varphi_{\rm H}, \theta_{\rm H}) = (-30^\circ, -60^\circ)$ near the edges of the operating envelope. At higher $\varphi_{\rm H}$, energy variation increases rapidly to $\Delta E_{\rho H} = 2.30 \text{ eV}$ by $(\varphi_{H}, \theta_{H}) = (+40^{\circ},$ 0°) at the outermost edge of the recommended range, with the desired H28 abstraction reaction now endoergic and failing to occur at most values of $\rho_{\rm H}$. Besides becoming taller, the PES grows more symmetrical and wider at the higher-energy peaks with the lower-energy valleys getting more sharply defined and narrower at larger $\varphi_{\rm H}$. Most

importantly, the three critical values for $\rho_{\rm H}$ that produce minimum net reaction energy and ensure desired reaction exoergicity apparently do not vary with $\varphi_{\rm H}$ at workable values of $\theta_{\rm H}$. Thus by operating at or near these three critical values ($\rho_{\rm H} = 0^{\circ}$, 120°, and 240°), the experimentalist can be assured of optimal reaction exoergicity throughout the entire recommended ($\varphi_{\rm H}$, $\theta_{\rm H}$) working range of ~ (±40°, ±80°) for Reaction II.

4.5. Lateral Displacement Error Tolerance

To determine the maximum tolerable lateral misplacement error of GeRad2 that will still result in a successful consummation of Reaction II, we start by defining the $U_{\rm H}$ -axis as a vector pointing from $O'_{\rm H}$ to C59 and the $V_{\rm H}$ -axis (not shown) as a vector originating at $O_{\rm H}^\prime$ and perpendicular to $U_{\rm H}$ that points parallel and codirectional with a vector from C66 to C74 (Fig. 24). We can then examine whether the Ge65-H28 bond still forms when GeRad2 is translationally displaced within the $U_{\rm H}V_{\rm H}$ plane away from its intended position at any point within a particular approach trajectory. The present work analyzes a representative reaction point ($R_{\rm H} = 5.80$ Å) along a single exemplar approach trajectory: $(\varphi_{\rm H}, \theta_{\rm H}, \rho_{\rm H}) = (0^{\circ}, 0^{\circ}, 0^{\circ})$. The lateral displacement of GeRad2 from its intended trajectory is reported as a displacement angle δ_{H} measured from U_{H} and a displacement radial distance $\Delta r_{\rm H}$ measured from O'_H.

Simulations began by examining small $\Delta r_{\rm H}$, moving to bigger $\Delta r_{\rm H}$, simulating progressively larger displacement error circles. At some $\Delta r_{\rm H}$ we would expect to find that Ge65 and H28 are too far apart to form the desired bond to consummate the abstraction. With GeRad2 positioned at $R_{\rm H} = 5.80$ Å, where tooltip and workpiece are just near enough for the H28 abstraction to begin to occur, reaction failure first occurs at $\Delta r_{\rm H} = 0.5$ Å but only for $\delta_{\rm H} =$ $150^{\circ}-210^{\circ}$. At $\Delta r_{\rm H} = 0.6$ Å the failure occurs at a greater range of $\delta_{\rm H}$; by $\Delta r_{\rm H} \ge 0.7$ Å, failure occurs at all angles $\delta_{\rm H} = 0^{\circ}-360^{\circ}$ tested full circle at 30° increments. This error tolerance is slightly less generous than the 0.5 Å



Fig. 23. PES for Reaction II as a function of tooltip rotational angle $\rho_{\rm H}$, for $R_{\rm H} = 5.80$ Å at various combinations of $\varphi_{\rm H}$ and $\theta_{\rm H}$.



Fig. 24. Geometry used for displacement error tolerance with HAbstH-GeRad complex shown at left and GeRad2 shown at right, in position to consummate Reaction II; $\Delta r_{\rm H}$ and $\delta_{\rm H}$ are defined as the radial and angular displacement of GeRad2 relative to its "ideal" entry position at $\varphi_{\rm H} = 0^{\circ}$, $\theta_{\rm H} = 0^{\circ}$. (C = yellow, H = blue, Ge = white).

tolerance found in Reaction I (Section 3.5), in part because the Ge–H bondlength (1.53 Å) is shorter than the Ge–C bondlength (1.95 Å) but mainly because the error tolerance is sensitively a function of $R_{\rm H}$. Moving GeRad2 slightly closer to H28 dramatically increases the lateral displacement error tolerance, producing a much larger Δr cutoff value for achieving a successful H28 abstraction. For example, the maximum tolerable displacement error increases from $\Delta r_{\rm H} = 0.4$ Å at $R_{\rm H} = 5.80$ Å to $\Delta r_{\rm H} = 1.4$ Å at $R_{\rm H} = 5.60$ Å for all angles $\delta_{\rm H} = 0^{\circ} - 360^{\circ}$ tested full circle at 30° increments. At higher temperatures the practical lateral displacement error tolerance might be somewhat higher than predicted by 0 K simulations because the hydrogen transfer barrier can be more easily surmounted by thermal fluctuations. Note that the G65-C11 crossbonding pathology (Section 4.3) is not observed because on a $(\varphi_{\rm H}, \theta_{\rm H}, \rho_{\rm H}) = (0^{\circ}, 0^{\circ}, 0^{\circ})$ trajectory with GeRad2 positioned at $R_{\rm H} = 5.80$ Å and an error displacement of $\Delta r_{\rm H} = 0.5$ Å with $\delta_{\rm H} = 0^{\circ}$ (angle of closest approach) the Ge65–C11 distance is 4.36 Å, far beyond both the Ge–C equilibrium bondlength of 1.95 Å and the Ge-C Morse bond instability distance of 2.32 Å (Section 4.3).

4.6. Optimal Tooltip Trajectories

The optimal GeRad2 tooltip trajectory for Reaction II appears to be $(\varphi_{\rm H}, \theta_{\rm H}, \rho_{\rm H}) = (0^{\circ}, 0^{\circ}, 0^{\circ})$, although any approach trajectory within the recommended $(\varphi_{\rm H}, \theta_{\rm H})$ operating range of ~ $(\pm 40^{\circ}, \pm 80^{\circ})$ should suffice almost equally well if $\rho_{\rm H} = 0^{\circ}$. Reaction II is likely to be barrierless within the recommended operating range. After the abstraction of H28 is complete, the nonreactive hydrogenated GeRad2-H tool may then be withdrawn from the system along any noncollisional trajectory that is convenient, preferably $(\varphi_{\rm H}, \theta_{\rm H}, \rho_{\rm H}) = (0^{\circ}, 0^{\circ}, 0^{\circ}).$

A GeRad2 tool started at $(\varphi_{\rm H}, \theta_{\rm H}, \rho_{\rm H}) = (0^{\circ}, 0^{\circ}, 0^{\circ})$ and rotated in $\varphi_{\rm H}$ will encounter a nonreactive increasingly repulsive barrier (rising to >3 eV) blocking further travel at $\varphi_{\rm H} > +40^{\circ}$ near $R_{\rm H} = 5.80$ Å, whereas at $\varphi_{\rm H} < -40^{\circ}$ near $R_{\rm H} = 5.80$ Å the tool will encounter no significant repulsive barrier and will proceed to pathological Ge65-C11 bonding, immobilizing both tool and workpiece without abstracting H28. Because the Ge-C bond is the weakest in the system, tool and workpiece could then be pulled apart, mechanically reversing the Ge65-C11 pathology without permanent damage to either structure, but the exit trajectory would have to be carefully controlled to avoid unpredictably altering the state of H28 bonding during the exit. Thus the operation of GeRad2 near $R_{\rm H} = 5.80$ Å may be said to be "repulsive" for $\varphi_{\rm H} > +40^{\circ}$ (toward GeRad) but "sticky" for $\varphi_{\rm H} < -60^{\circ}$ (toward HAbstH).

5. REACTION III: DETACH GeRad TOOL FROM RECHARGED HAbst TOOL

In Reaction III of the HAbst recharge reaction sequence RS5 (Fig. 1), mechanical energy is applied to the first GeRad tool to pull it away from the tip-dehydrogenated HAbst tool, breaking the Ge35–C12 bond (required tensile force $\sim 3.64 \text{ nN}$)⁷ to recover the original GeRad tool with a radical site on atom Ge35 while leaving behind a recharged active HAbst tool with a radical site on the distal ethynyl carbon atom C12. The carbon–carbon bond order in the C₂ ethynyl group remains at 3.

After defining the tooltip geometry and coordinate system for Reaction III (Section 5.1) we calculate the reaction PES (potential energy surface) as a function of rotational angle ρ_D of the departing GeRad tool (Section 5.2) and as a function of departure positional angles φ_D and θ_D (Section 5.3), describe trajectory-related pathologies (Section 5.4), then recommend some optimal GeRad tooltip departure trajectories for this reaction (Section 5.5).

5.1. Tooltip Geometry and Coordinate System

The tooltip geometry and coordinate system for Reaction III is shown in Figure 25. This coordinate system is defined by fixing positions of atoms that are most closely under the control of the experimentalist. The leftmost image in Figure 25 defines the HAbst-GeRad tooltip orientation angle beta (β), which is the angular displacement of the O"-normal vector (pointing from O' to O") from the X-axis—or more specifically, the angle between the O-normal vector (aka. X-axis) and the O"-normal vector. Illustrated here is the $\beta = 79.04^{\circ}$ case which obtains at the completion of Reaction II. The same geometry is found when H28 is deleted from the HAbstH-GeRad complex at



REVIEW

Fig. 25. Coordinate system for Reaction III: The image at left defines the HAbst-GeRad tooltip orientation angle beta (β), which is the angular displacement of the O"-normal vector (pointing from O' to O") from the *X*-axis ($\beta = 0^{\circ}$ upon alignment with *X*-axis, $\beta = 79.04^{\circ}$ in image at left). In the image at right, the (*X*, *Y*, *Z*) coordinate system from Reaction I is translated to O", defining the congruent (X_D , Y_D , Z_D) coordinate system. Displacement of the positionally controlled GeRad tooltip from O" to O_D by a distance R_D during Reaction III is described by the similarly-defined φ_D , θ_D , and ρ_D displacement angles. (C = yellow, H = blue, Ge = white).

the end of Reaction I ($\varphi = 50^{\circ}$, $\theta = 70^{\circ}$, $\rho = 20^{\circ}$, R = 4.85 Å) and the resulting structure is optimized with the 3 control atoms on each handle fixed. Changing β alters the energy of the HAbst-GeRad complex via some combination of bond-bending strain and handle-handle steric interaction. Figure 26 shows that system energy rises with β and that the collinear (GeRad aligned with X-axis) configuration at $\beta = 0^{\circ}$ has the lowest energy (taken as $E_{\min} = 0$ eV). The minimum system energy E_{\min} at each bend angle β occurs at a different O''-O' separation (R_{\min})



Fig. 26. Minimum system energy E_{\min} at each HAbst-GeRad bend angle β occurs at a particular O''-O' separation (= R_{\min}) which also progressively rises with β in Reaction III. E_{\min} and R_{\min} for each β were identified using structure optimizations at a series of separations at $\rho_{\rm D} =$ 20°. Inset chart shows energy versus tool displacement distance $R_{\rm D}$ for the collinear $\beta = 0^{\circ}$ trajectory.

which also progressively rises with β . Most values of $\beta > 90^{\circ}$ are excluded due to tool handle proximity.

In the rightmost image of Figure 25, the (X, Y, Z) coordinate system from Reaction I is translated to O", defining the congruent (X_D, Y_D, Z_D) coordinate system for GeRad departure. Movement of the positionally controlled GeRad tooltip from O" to the displaced origin O_D by a distance R_D during Reaction III is described by the φ_D , θ_D , and ρ_D displacement angles that are defined similarly as for φ , θ , and ρ in Reaction I (Fig. 2, Section 3.1). Note that at the start of Reaction III, C1 no longer lies exactly at O' on the X-axis line but has moved a distance 0.0205 Å from the X-axis line. Similarly, Ge35 has moved 0.067 Å away from the O"-normal vector—the vector that passes through O" and lies perpendicular to the C30/C32/C34 plane. After Reaction III is completed, C12 is displaced 0.71 Å from origin O' in the final H28-removed configuration.

Only four of the six possible degrees of freedom in GeRad departure trajectories are considered here. Pitch and yaw rotations during GeRad retraction are beyond the scope of this present work because they would greatly increase the complexity and computational cost of the analysis but are of uncertain utility because significant motion in these dimensions is less likely to be readily accessible experimentally for Reaction III.

5.2. PES as a Function of Rotational Angle $\rho_{\rm D}$

The PES as a function of rotational angle ρ_D (i.e., twirling GeRad around its central axis, the O"-normal vector) is



Fig. 27. Energy as a function of $\rho_{\rm D}$ at R = 4.85 Å, for $\beta = 0^{\circ}$ using $(\varphi, \theta) = (0^{\circ}, 0^{\circ})$ and for $\beta = 79.04^{\circ}$ using $(\varphi, \theta) = (+50^{\circ}, +70^{\circ})$ in Reaction III.

shown in Figure 27. In the collinear configuration of HAbst-GeRad at $\beta = 0^{\circ}$, the energy variation for an entire repeating cycle of rotation of the threefold-symmetric GeRad tooltip from $\rho_{\rm D} = 0^{\circ}-120^{\circ}$ is less than 0.01 eV, rising at $\beta = 79.04^{\circ}$ to only ± 0.06 eV (similar to results in Fig. 7), both below the 0.14 eV limit of computational accuracy (Section 2) for this method. The PES minimum for the $\beta = 79.04^{\circ}$ configuration occurs near $\rho_{\rm D} = 20^{\circ}$, the setting mostly used in the following analyses, but choice of $\rho_{\rm D}$ has only limited impact on reaction energetics.

Note that in Figure 27 the $\beta = 0^{\circ}$ PES curve lies about ~ 0.4 eV higher in energy than the $\beta = 79.04^{\circ}$ curve even though the $\beta = 0^{\circ}$ PES curve is ~ 0.6 eV lower in Figure 26—the $\beta = 0^{\circ}$ curve in Figure 27 is taken at suboptimal R = 4.85 Å whose energy lies ~ 1 eV higher than the 4.15 Å optimal R for $\beta = 0^{\circ}$.

5.3. PES as a Function of Positional Angles $\varphi_{\rm D}$ and $\theta_{\rm D}$

The peak PES as a function of positional angles $\varphi_{\rm D}$ and $\theta_{\rm D}$ for $\beta = 79.04^{\circ}$ is shown in Figure 28. (For convenience, $\theta_{\rm D} = -180^{\circ}$ points are replotted at +180°.) To obtain each point, representing a unique departure trajectory, the tools were locked at the indicated $(\varphi_{\rm D}, \theta_{\rm D})$ rotational position with $\rho_{\rm D} = 20^\circ$, then $R_{\rm D}$ was increased stepwise from 0 Å to as much as 7.1 Å using variable step increments of between 0.3-0.5 Å until either breakage of the Ge35–C12 bond (blue squares) or a reaction pathology (yellow squares; Section 5.4) occurred during the restricted geometry optimization at each step. Both singlet and triplet PES were calculated, but singlet-triplet transition probabilities at singlet-triplet PES approach points are difficult to estimate, so for convenience the endpoint of Reaction III is presumed to occur when the computed spin density of Ge35 reaches a significant (>0.5) level. Figure 28 shows the maximum energy $E_{\rm max}$ of the system at the given $\varphi_{\rm D}$ and $\theta_{\rm D}$ (likely occurring near the last step yielding Ge35– C12 bond scission), along with the separation distance

 R_{max} at which E_{max} occurs. E_{max} varies from 4.8–9.7 eV, indicating significant differences among useful trajectories that well exceed the expected DFT computational error. R_{max} spans a relatively large range in part because of the mobility and extensibility of the Ge35–C12–C11–C1 chain. Figure 29 shows a representative trajectory at (φ_{D} , θ_{D} , ρ_{D}) = (0°, 0°, 20°) and β = 79.04° for Reaction III, a trajectory having the lowest E_{max} in Figure 28.

The relatively high energies reported near the borderline of pathological trajectories result in part from the forcing of large ethynyl deflection angles prior to Ge35-C12 bond scission but may also include an artifactual component due to computational limitations, as follows. Reaction III imposes rotational forces on the HAbst tooltip, but full rotation is prevented by the fixed atoms in the base, resulting in overall handle deformation and significant bond stretching near the fixed atoms. For example, at $(\varphi_{\rm D}, \theta_{\rm D}) = (+150^\circ, +30^\circ)$ for $R_{\rm D} = 6.6$ Å just prior to bond scission the C6–C7 bond (1.83 Å, +19% strain) and the C6–C5 bond (1.80 Å, +17% strain) in the HAbst handle are highly stretched, just below the Morse potential inflection point at 1.87 Å (+21% strain) where the C–C bond becomes mechanically unstable, driving up apparent tooltip system energy. However, in an actual DMS tool the tooltip base atoms are not fixed but are free to move and thus can evenly redistribute the bond strain from the frontline cage back into deeper cages, reducing both tooltip energy and the risk of handle bond breakage in an actual tool during normal use.

The probability of reaction pathology is minimized when the mechanical dissociation of the Ge35–C12 bond compels the remaining bonds to dissipate the least possible energy. The lowest E_{max} and R_{max} are found at (φ_D , θ_D , ρ_D) = (0°, 0°, 20°), with Ge35–C12 bondbreaking occurring at a separation distance of $R_D \sim 3.1$ Å with a bond scission energy of ~4.8 eV. This trajectory runs parallel to the O-normal vector (i.e., to both +X and +X_D coordinate axes).

The peak PES as a function of positional angles $\varphi_{\rm D}$ and $\theta_{\rm D}$ for $\beta = 0^{\circ}$ is shown in Figure 30, obtained and prepared similarly to Figure 28. $E_{\rm max}$ varies only moderately from 4.9–6.2 eV across a broad range of useful trajectories ($\varphi_{\rm D}$, $\theta_{\rm D}$, $\rho_{\rm D}$) = ($\pm 90^{\circ}$, $\pm 60^{\circ}$, 20°). These energies are generally higher than the 4.8 eV values for the best trajectories at $\beta = 79.04^{\circ}$ because at $\beta = 0^{\circ}$ the system energy is reduced by ~0.6 eV (much of it removed from the now-unstrained Ge35–C12 bond; Fig. 26), hence extra energy must be mechanically applied to the collinear Ge35–C12 bond to induce this bond to break as compared to the $\beta = 79.04^{\circ}$ case.

5.4. Trajectory Pathologies of Reaction III

At $\beta = 79.04^{\circ}$ (Fig. 28) there are 14 unusable trajectories (Table III) among the 60 unique trajectories at



Fig. 28. Peak system energy prior to bondbreaking E_{max} (top) and the separation distance at which E_{max} occurs R_{max} (bottom) as a function of (φ_D , θ_D) for $\beta = 79.04^{\circ}$ and $\rho_D = 20^{\circ}$ in Reaction III. Blue and green values keyed to scale bar below each chart; yellow areas indicate pathological outcomes; gray areas indicate geometrically unfavorable configurations that were excluded.



Fig. 29. Energy versus separation distance $R_{\rm D}$ for singlet energy of geometry optimized singlet ("Singlet") and for triplet energy of geometry optimized singlet ("Triplet"), for $(\varphi_{\rm D}, \theta_{\rm D}, \rho_{\rm D}) = (0^{\circ}, 0^{\circ}, 20^{\circ})$ at $\beta = 79.04^{\circ}$ in Reaction III.

30° angular resolution for the range $(\varphi_{\rm D}, \ \theta_{\rm D}, \ \rho_{\rm D}) =$ $(\pm 180^\circ, \pm 60^\circ, 20^\circ)$. In this coordinate system there is no reason to expect pathologies to be symmetrical around $\varphi_{\rm D} = 0^{\circ}$; the relative position of the tools makes HAbst more likely to interfere with GeRad motion at $\varphi_{\rm D} < 0^{\circ}$. In 3 instances (gray squares, Fig. 28), the trajectory is excluded because the motion of Ge35 carries it toward C12 (such that C12 or other HAbst atoms would geometrically lie inside the GeRad cage if GeRad was moved along the trajectory without optimization), not away as is required for the consummation of Reaction III. Among the remaining 57 trajectories, there are 11 unique pathological trajectories (yellow squares, Fig. 28) comprising six different classes for Reaction III as shown in Figure 31, including: (A) ethynyl insertion into the HAbst handle cage (4 instances), (B) Ge35-C11 bonding (3 instances),



Fig. 30. Peak system energy prior to bondbreaking E_{max} (top) and the separation distance at which E_{max} occurs R_{max} (bottom) as a function of (φ_{D} , θ_{D}) for $\beta = 0^{\circ}$ and $\rho_{\text{D}} = 20^{\circ}$ in Reaction III. Blue and green values keyed to scale bar below each chart; yellow areas indicate pathological outcomes; gray areas indicate geometrically unfavorable configurations that were excluded.

(C) Ge35–C2 bonding (1 instance), (D) C5–C6 bond break in the HAbst handle cage (1 instance), (E) Ge35–C36 shoulder separation in GeRad tooltip (1 instance), and (F) hydrogen abstraction by C12 after Ge35–C12 bond scission (1 instance). This leaves 46 unique nonpathological trajectories potentially available for Reaction III at 30° angular resolution for the range (φ_D , θ_D , ρ_D) = (±180°, ±60°, 20°). It is possible but unlikely that additional significant pathologies might be found using a smaller angular resolution, a smaller step size, or by extending the range of θ_D to ±90°; even a small reaction barrier to an unrecognized pathology might suffice to allow the geometry optimization algorithm to avoid it, whereas in a physical system thermal vibrations could surmount a small barrier and permit the pathology to occur. Alternatively, some existing pathologies may prove inaccessible if sufficient energy barriers are found at higher resolution (a subject for future study).

Pathology D is the only trajectory that produces a bonding alteration in the HAbst handle that is unrelated to ethynyl reactivity and appears to be the only pathology directly related to the proximity of HAbst and GeRad handle atoms during the reaction. (The motion of GeRad handle atom C36 and its hydrogens apparently pushes HAbst

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$\varphi_{\rm D}~({\rm deg})$	$\theta_{\rm D}~({\rm deg})$	Pathology (Type)	$R_{\rm D}$ of pathol. Å
-180	-60	Ge35 motion toward C12	_
-150	-60	Ge35 motion toward C12	_
-120	-60	Ge35 motion toward C12	—
-180	0	Ge35-C2 bonding (C)	4.1
-180	-30	Ge35-C11 bonding (B)	2.2
-150	0	shoulder separation (E)	5.6
-150	-30	Ge35-C11 bonding (B)	2.2
-120	-30	C5–C6 bond breaking (D)	6.1
-90	-60	Ethynyl insertion (A)	4.1
-60	-60	Ethynyl insertion (A)	4.1
-30	-60	Hydrogen abstraction (F)	6.6
+120	-60	Ethenyl insertion (A)	3.6
+150	-30	Ge35–C11 bonding (B)	2.2
+150	-60	Ethenyl insertion (A)	3.6

Table III. Pathological departure trajectories ($\varphi_{\rm D}$, $\theta_{\rm D}$) at $\rho_{\rm D} = 20^{\circ}$, for $\beta = 79.04^{\circ}$ in Reaction III.

handle atom C5 away from the fixed C4 atom, although this pathology could be artifactual since a fixed atom is involved and in a real handle this atom would be free to move to relieve the strain.) Significant distortion of handle shapes is observed around the endpoint of many trajectories but there are no handle collision problems as reported above for Reaction I (Section 3.3), probably because the stepwise procedure employed here allows handles to adjust their shape (sometimes to a significant extent).

The details of two of the six pathologies are influenced by choice of $\rho_{\rm D}$. For pathology *E* at $(\varphi_{\rm D}, \theta_{\rm D}) = (-150^\circ,$ 0°), the only pathology that yields bonding alterations in the GeRad handle, one entire repeating cycle of rotation of the threefold-symmetric GeRad tooltip from $\rho_{\rm D} = 0^{\circ} - 120^{\circ}$ was examined stepwise for $R_{\rm D} \ge 2.2$ Å in 0.4 Å increments until the pathology occurred at a separation distance $R_{\rm D} =$ R_{path} . Table IV shows that Pathology E cannot be avoided by choice of $\rho_{\rm D}$ but occurs at different separations $R_{\rm path}$ ranging from 4.6-6.6 Å. From a similar study of pathology F at $(\varphi_{\rm D}, \theta_{\rm D}) = (-30^\circ, -60^\circ)$, Table IV shows that outright abstraction of a hydrogen atom from the GeRad cage occurs at three $\rho_{\rm D}$ settings within the $\rho_{\rm D} = 0^{\circ} - 120^{\circ}$ range, while at other $ho_{
m D}$ settings the distance of closest approach between the distal ethynyl radical site at atom C12 and the nearest H atom on the GeRad comes within $R(H)_{min} =$ 1.68–1.94 Å. This is larger than the 1.09 Å equilibrium



Fig. 31. Six classes of pathological trajectory in Reaction III. (C = yellow, H = blue, Ge = white).

bondlength for C–H or the 1.46 Å Morse inflection point separation⁵ for C–H. However, the 1.68–1.94 Å range lies mostly within the 1.84 Å intercarbon distance for a transitional linear C–H–C system in which both C–H bonds are stretched to their Morse inflection point limits (and the Morse limit for C–C is 1.87 Å), hence the absence of thermally-accessible abstraction events for Pathology *F* at these alternative ρ_D settings cannot be guaranteed. Analogous rotation of the HAbst tool appears equally unlikely to cure Pathology *C* at (±180°, 0°). It should also be noted that since all known pathologies are clustered in the same (φ_D , θ_D) region, the avoidance of one class of pathology may increase the susceptibility to another class.

During Reaction III, GeRad moves relatively long distances (3.5 Å and more) and a lot of energy is put into the system to break the Ge35-C12 bond. Optimization runs initiated near an endpoint separation geometry can yield spurious pathological outcomes that disappear when the structure is stepped through a physically more realistic series of smaller displacements, allowing atoms to adjust their positions in response to the more slowly changing configuration. For example, a $(\varphi_{\rm D}, \theta_{\rm D}) = (+150^\circ, 0^\circ)$ trajectory started at $R_{\rm D} = 2.2$ Å immediately proceeds to Pathology B, whereas initiating the same trajectory stepwise from $R_{\rm D} = 0$ Å to 2.2 Å allows the C1–C11–C12 angle to bend and other bonds to stretch to accommodate GeRad movement while keeping the Ge35-C12 bond intact. Similarly, an ethynyl insertion into the GeRad cage that was observed for a $(\varphi_D, \theta_D) = (-30^\circ, -60^\circ)$ trajectory started at $R_{\rm D} = 2.2$ Å (for most $\rho_{\rm D}$ settings) disappeared using stepwise calculations started from $R_{\rm D} = 0$ Å.

Choice of ρ_D does not significantly influence the overall energetics of Reaction III but can affect the distribution of peak bond strains and thus slightly alter the probability of a pathological outcome. Retraction of GeRad transmits a tensile load from the Ge35–C12 bond to the Ge35–C36,

Table IV. Effect of $\rho_{\rm D}$ on the separation distance $R_{\rm path}$ at which the shoulder separation pathology *E* at $(\varphi_{\rm D}, \theta_{\rm D}) = (-150^\circ, 0^\circ)$ occurs and on the distance R(H)_{min} between the C12 radical and the nearest H atom during the abstraction pathology *F* at $(\varphi_{\rm D}, \theta_{\rm D}) = (-30^\circ, 60^\circ)$, for $\beta = 79.04^\circ$ in Reaction III.

$\rho_{\rm D}$ (deg)	Pathology <i>E</i> <i>R</i> _{path} (Å)	Pathology <i>F</i> R(H) _{min} (Å)
0	6.1	1.85
10	6.1	1.72
20	5.6	abstraction
30	5.1	1.68
40	4.6	1.79
50	4.6	1.94
60	5.1	abstraction
70	5.6	1.7
80	6.6	1.9
90	6.1	1.83
100	6.1	1.76
110	6.1	abstraction
120	6.1	1.85

Table V. Pathological departure trajectories (φ_D , θ_D) at $\rho_D = 20^\circ$, for = 0° in Reaction III.

$\varphi_{\rm D}$ (deg)	$\theta_{\rm D}$ (deg)	Pathology (Type)	$R_{\rm D}$ of pathol. (Å)
-180	0	Ge35 motion toward C12	_
-180	-30	Ge35-C11 bonding (B)	2.8
-180	+30	Ge35-C11 bonding (B)	2.8
-150	-30	Ge35-C11 bonding (B)	4.3
-150	0	Ge35-C11 bonding (B)	3.3
-150	+30	Ethynyl insertion (A)	5.3
+150	-30	Ge35-C11 bonding (B)	4.3
+150	0	Ge35-C11 bonding (B)	3.3
+150	+30	Ge35–C11 bonding (B)	4.3

Ge35-C37 and Ge35-C38 shoulder bonds of the GeRad tool. The special case of a departure trajectory that is parallel to the O"-normal vector produces an approximately equal tensile force on all three shoulder bonds, but in all other cases the trajectory is imperfectly aligned with this axial line and generates an asymmetric stretch force distribution that is necessarily more concentrated on just one or two shoulder bonds rather than all three. The risk of a shoulder separation event (Pathology E) is slightly higher when the stretch force is concentrated on a single shoulder bond and slightly lower when that force is evenly distributed over two shoulder bonds. For example, on the ($\varphi_{\rm D}$, $\theta_{\rm D}$ = (0°, 0°) trajectory a setting of $\rho_{\rm D}$ = 20° concentrates the tensile force on a single Ge35-C38 shoulder bond, stretching it to 2.15 Å (+9% bond strain) immediately prior to Ge35–C12 bond scission; a setting of $\rho_{\rm D} = 80^{\circ}$ distributes force evenly over the two Ge35-C37 and Ge35-C38 shoulder bonds, reducing their individual peak stretch to 2.09 Å (+6% bond strain) while producing only -1.3%bond compression in Ge35-C36 (cf. the 2.32 Å (+19% bond strain) Morse limit for Ge–C bond instability.)

At $\beta = 0^{\circ}$ (Fig. 30) there are 9 unusable trajectories at 30° angular resolution in the range ($\varphi_{\rm D}$, $\theta_{\rm D}$, $\rho_{\rm D}$) = (±180°, ±60°, 20°)—one excluded trajectory and 8 pathological trajectories including 1 instance of Pathology *A* and 7 instances of Pathology *B* (Table V)—leaving 51 unique nonpathological trajectories potentially available for Reaction III.

5.5. Optimal Tooltip Trajectories

The optimal GeRad detachment trajectory for Reaction III appears to be $(\varphi_{\rm D}, \theta_{\rm D}, \rho_{\rm D}) = (0^{\circ}, 0^{\circ}, 20^{\circ})$ at $\beta = 79.04^{\circ}$, with Ge35–C12 bondbreaking occurring near a separation distance of $R_{\rm D} \sim 3.1$ Å with a bond scission energy of ~4.8 eV. This trajectory is aligned with the X and $X_{\rm D}$ coordinate axes (paralleling the C1–C11–C12 final equilibrium geometry of the recharged HAbst tool) and has the highest probability of reaction completion and safety because it offers the lowest bond dissociation energy and the shortest tooltip travel distance hence the quickest release (lowest $R_{\rm max}$), and also occupies a position on the (φ_D, θ_D) peak PES that is maximally distant from all known pathologies. Bond scission energies are similar for alternative trajectories that lie within $\pm 30^{\circ}$ of the optimal one, although the bond breaking separation distance is ~1 Å longer for $\theta_D = -30^{\circ}$ trajectories as compared to $\theta_D = +30^{\circ}$ trajectories. It is desirable to have multiple viable trajectories available since in a particular experimental setup some range of $(\varphi_D, \theta_D, \rho_D)$ settings might not be accessible at all or might be easier to attain than others. The $(0^{\circ}, 0^{\circ}, 20^{\circ})$ trajectory requires no experimentally challenging rotational motions, only translational motions, while GeRad is still bonded to HAbst.

The $(0^{\circ}, 0^{\circ}, 20^{\circ})$ trajectory makes good use of the effective pre-weakening of the Ge35–C12 bond that occurs at near-maximum bond bending at $\beta = 79.04^{\circ}$. By contrast, in the collinear configuration at $\beta = 0^{\circ}$ the system energy is reduced by 0.6 eV (much of it removed from the now-unstrained Ge35–C12 bond), which means that this extra amount of energy additionally must be mechanically applied to the collinear Ge35–C12 bond to induce this bond to break.

6. CONCLUSIONS

REVIEW

The use of precisely applied mechanical forces to induce site-specific chemical transformations is called positional mechanosynthesis, and diamond is an important early target for achieving mechanosynthesis experimentally. A key step in diamond mechanosynthesis (DMS) employs an ethynyl-based hydrogen abstraction tool (HAbst) for the site-specific mechanical dehydrogenation of the H-passivated diamond lattice surface, creating a radical site that can accept adatoms via radical-radical coupling in a subsequent positionally controlled reaction step. The tool, once used, may be recharged by removing the abstracted hydrogen atom from the tool, using a positionally controlled reaction sequence involving three sequential reactions. In this paper we undertake the first study of tool-workpiece operating envelopes and optimal tooltip trajectories for positionally controlled DMS tools, in this case a complete three-reaction recharge reaction sequence for HAbstH/HAbst. The results of our study may help to define equipment and tooltip motion requirements that are needed to execute the proposed reaction sequence experimentally.

The optimal GeRad approach trajectory for Reaction I continuously maintains an acceptably low net reaction energy throughout the entire reaction process, allowing tool and workpiece to be positioned in the energy landscape on a valley floor of adequate depth but maximum width which permits successful consummation of Reaction I even in situations where tooltip placement error may be significant. Examples include the (φ , θ , ρ) = (+40°, +70°, +40°) and (+50°, +70°, +20°) approach trajectories that minimize demands on the reliability of an

experimental positional control system, since the controls can be set once at the start of the reaction and held constant through its conclusion. Various alternative compound, low-barrier and other trajectories are also useful in certain circumstances.

The optimal GeRad2 approach trajectory for Reaction II appears to be $(\varphi_{\rm H}, \theta_{\rm H}, \rho_{\rm H}) = (0^{\circ}, 0^{\circ}, 0^{\circ})$, although any approach trajectory within the recommended $(\varphi_{\rm H}, \theta_{\rm H})$ operating range of ~ $(\pm 40^{\circ}, \pm 80^{\circ})$ should suffice almost equally well if $\rho_{\rm H} = 0^{\circ}$. Reaction II is likely to be barrierless within the recommended operating range.

The optimal GeRad detachment trajectory for Reaction III appears to be $(\varphi_D, \theta_D, \rho_D) = (0^\circ, 0^\circ, 20^\circ)$ at $\beta = 79.04^\circ$, with Ge35–C12 bondbreaking occurring at a separation distance of $R_D \sim 3.1$ Å with a bond scission energy of ~4.8 eV. This trajectory has the highest probability of reaction completion and safety among neighboring alternatives because it offers the lowest bond dissociation energy, the quickest release (lowest R_{max}), and a position on the (φ_D, θ_D) peak PES that is maximally distant from all known pathologies.

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